Catarina Monteiro Pinto

A Forensic (Chemical) Analysis of Portuguese Postage Stamps (1857-1909)

Mestrado em Química Forense

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Universidade de Coimbra

Catarina Monteiro Pinto

A Forensic (Chemical) **A**nalysis of **P**ortuguese **P**ostage **S**tamps (1857-1909)

Dissertação apresentada para provas de Mestrado em Química Forense

Orientador: Prof. Dr. J. Sérgio Seixas de Melo

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“Great things are done by a series of small things brought together.”

Vincent Van Gogh

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Index

Chapter I – Introduction

Chapter II – Experimental Methods

Chapter III – Results and Discussion

Chapter IV – Conclusions

Appendix

Index of Figures

Chapter I – Introduction

Chapter II – Experimental Methods

Chapter III – Results and Discussion

Index of Tables

Chapter I – Introduction

Chapter III – Results and Discussion

Abbreviations

A	Absorbance
C	Concentration
$[M-H]^-$	Deprotonated Molecular Ion
DAD	Diode Array Detector
DMSO	Dimethylsulfoxide
ESI	Electrospray Ionization
EDXRF	Energy Dispersive X-ray Fluorescence
S_n	Excited State
ε	Extinction Coefficient
FTIR-ATR	Fourier Transform Infrared-Attenuated Total Reflectance
C_i	Fractional Contribution
S_0	Ground State
HPLC	High-Performance Liquid Chromatography
HPLC-DAD	High-Performance Liquid Chromatography-Diode Array Detector
HPLC-MS	High-Performance Liquid Chromatography-Mass Spectroscopy
I_a	Intensities of Absorbed Light
I_e	Intensities of Emitted Light
τ_F	Life Time Fluorescence
LC-HRMS	Liquid Chromatography-High Resolution Mass Spectroscopy
$MeOH:H_2O$	Metanol:Water
MS	Mass Spectroscopy
l	Path Length
A_i	Pre-exponential Factor
Φ_F	Quantum Yield of Fluorescence
m/z	Ratio mass/charge
T_1	Triplet State of Lowest Energy
t_r	Retention Time
UV	Ultraviolet
UV-Vis	Ultraviolet-Visible
λ	Wavelength
λ_{em}	Wavelength of Emission

λ_{exc}	Wavelength of Excitation
λ_{max}	Wavelength maxima
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

Resumo

A natureza dos pigmentos ou corantes usados para imprimir os primeiros selos postais portugueses permaneceu desconhecida até agora. A partir de uma análise anterior de alguns selos postais do Reino Unido, sabemos que o ácido carmínico, a cochonilha, (para os vermelhos) e a icónica mauveína (para lilás / roxo) foram utilizados no período de 1847 a 1901. Neste trabalho, foi realizado um estudo das tintas usadas para as cores vermelha, rosa, roxa e laranja num número selecionado de selos postais portugueses do período 1857-1909. Este estudo foi baseado em análises envolvendo uma variedade de técnicas (fluorescência de raios-X (XRF), espectroscopia UV-VIS, HPLC-DAD-MS, fluorescência no estado estacionário e resolvida no tempo). Verificou-se que as tintas incluíram, entre outros, pigmentos inorgânicos, tais como o cinábrio (HgS), óxido de chumbo (Pb_3O_4), cromato de chumbo ($PbCrO_4$), sulfeto de chumbo (PbS) e compostos orgânicos, entre os quais o ácido carmínico e a eosina Y. Este trabalho demonstrou ser possível a utilização de técnicas não-destrutivas para a identificação de algumas "moléculas da cor" envolvendo o XRF (para cinábrio, óxido de chumbo, cromato de chumbo, sulfeto de chumbo), absorção UV-Vis (para ácido carmínico e eosina Y) e espectros de fluorescência, juntamente com rendimentos quânticos e tempos de vida (para eosina Y).

Palavras-chave: Selos postais; HPLC-DAD-MS; Absorção UV-Vis; Fluorescência; HgS; Ácido Carmínico; Eosina Y; Corantes e Pigmentos.

Abstract

The nature of the pigments or dyes (molecules of colour) used to dye the first Portuguese postage stamps has remained unknown until now. From a previous analysis of some postage stamps from the United Kingdom it is known that carminic acid and Cochineal, for the red and the iconic mauveine for the lilacs / purple were used during the period 1847 to 1901. In this work, a study has been made regarding the inks used for red, rose, purple and orange colours in a selected number of Portuguese postage stamps from the period 1857-1909. This is based on the analysis involving a variety of techniques (X-Ray Fluorescence (XRF), UV-VIS spectroscopy, HPLC-DAD-MS, steady and time resolved fluorescence). It was found that the inks included, among others, the inorganic pigments cinnabar (HgS), lead oxide (Pb_3O_4) and chromate ($PbCrO_4$), lead sulfide (PbS), and the organic compounds carminic acid and eosin y. This work demonstrated non-destructive analysis methods for identification of some molecules of colour involving the XRF (for cinnabar, lead oxide, lead chromate, lead sulfide), the UV-Vis (for carminic acid and eosin y) and fluorescence spectra, together with quantum yields and lifetimes (for eosin y).

Keywords: Postage Stamps; HPLC-DAD-MS; UV-Vis Absorption; Fluorescence; HgS; carminic acid; eosin y; Dyes and Pigments.

Chapter I

Introduction

1.1 The Origin of the Postage Stamps

On the origin of the postage stamp, as it is nowadays known, is *Sir Rowland Hill* (figure 1.1.1), an Englishman born on December 3, 1795, in Kidderminster, former professor and Secretary of the General Mail.[1–3]

Figure 1.1.1 - *Sir Rowland Hill* (from ref. [3]).

Before Sir *Rowland*, the exchange of correspondence was carried out by letters containing two marks, a *nominal stamp* – (i) indicating the mailing sender and a *fixed stamp* – (ii) indicating the rate to be paid by the recipient according to the weight and distance travelled by the letter/correspondence. This method had, however, some disadvantages, since the recipient paid the fixed stamp. This lead to, the use of different strategies to avoid paying the associated costs, with however, not renouncing to read the message.[2]

There are several stories associated to *Rowland Hill*, describing the reason that lead to the proposal of a recast of the correspondence delivery.[1,2] One of the stories is that, on one afternoon by the year 1836, *Hill* was traveling through the Scottish lakes when he witnessed the delivery of correspondence to a young female tabernacle. She, after carefully observe the letter, refused to pay the postage, rejecting it. *Rowland*, in conversation with her, was able to discover that the letter contained symbols on the back. Therefore, the young woman managed to read the letter, without paying the equivalent of a weekly salary. This and other tricks would compromise the Crown resources.[2]

However, the invention of the postage-paid system and the subsequent issuance of labels, further were known as postage stamps, dates back to 1653, in Paris, when the French *Jean Jacques Renouard de Villayer* received permission from Louis XIV, on the 18 of July, to transport the letters.[1,3]

Villayer managed to install many mailboxes through the streets of Paris, and made it available to the public, this was the invention of the postage-paid system. Each letter had to be paid in advance by the sender and not by the recipient. The postage was represented by a "*postage paid ticket*". These only differed from the current ones because it was not glued to the letter. However, *Villayer*'s organization lasted only a short period of time, since the history reports that in 1662 it no longer existed.[1] In 1663, the same system was created in London, by *William Deckwra*.[1]

The first envelopes appeared at the end of the XVIII century (in 1784), emitted by the Post of the Austrian Empires. The envelopes did not remain for a long time, it was only in 1818 that they appear and circulated until the end of 1837. They were commonly known as "*cavallini*" or "*cavallotti*", because they had a horse in the front of it.[1,3]

Parallelly, in China, in 1823, the letters circulated temporarily enveloped with the following inscriptions: for internal use - “*por 3 sapecas, pode esta carta passar em todas as províncias da China e só parar nas fronteiras do oceano*”; and, for use abroad - “*por 10 sapecas pode esta carta atravessar todos os mares e grandes montanhas*”.[1]

In 1830, *Charles Whiting* addressed a proposal to the English Government to allow the sale to public of stamped bands called *go free*, but the proposal was not accepted.[1]

Between 1834 to 1838, the British *James Chalmers*, a bookseller and typographer in Dundee, came up with the idea of applying the sticker system. This consisted of manufacturing a postage stamp sheet, gummed on the back, where several different types of values were printed separately. In December 1837, this sheet was presented to the House of Commons, by the Deputy *Wallace*, who also failed to approve it.[1]

Lorenz Koschier was a native of Slovenia and an Austrian citizen. In 1836, he proposed to the Austrian government that the sender could pay the letter through the postage stamps. Two years earlier, *Koschier* had already approached *Galway* (an Englishman, friend of *Rowland Hill*) regarding this idea of letters with postage stamps.[1] Therefore, influenced by *Koschier*, *Hill* wrote his famous proposal in 1837 - "*The Postal Reform: Its Importance and Advantages*" - to the British Post Office, which earned it the title of "*Postage Stamp Father*".[1–3] During that same year, on 22 November, a committee was appointed, by the House of Commons, to study the proposal. It was not an easy approval given the oppositions to his project, standing out like main adversaries the *Earl of Lichfield*, *Colonel Maberly* - Secretary of the Post and *Sir Robert Peel* - Chief of the Conservative Party. On December 26 of 1839, the proposal was finally accepted by the Treasury.[1] After that, the "*Penny Postage Act*" was approved by the House of Commons and the Postal Stamp was created. The first postage stamp to circulate in the world was the "*penny black*", in May 1840 (figure 1.1.2).[2,3]

Figure 1.1.2 – The one black penny; the first Postage Stamp printed in the world (from ref. [1]).

Although the idea of the postage stamp, as it is nowadays accepted, did not start with *Hill*, it was him who introduced it to England and showed the viability and practical application of this new system, which could not be achieved by its predecessors. Therefore, his recognition as the father of the postage stamp came only in 1860, when Queen Victoria made him a Knight.[1,2]

"A Sir Rowland Hill devemos hoje a existência da Filatelia" (*cit in*: 9, p.18).

1.1.1 Philately

Philately, is the general term used in the study, examination and collecting of postage stamps. Currently accepted, the designation came into use in 1864 after the publication of an article by the French numismatist *Herpin* (figure 1.1.1.1), which considered the *Selomania* (designation term) as humiliating and odious. Thus, "*Philatélie*" was proposed to represent the science of the postage stamps, from Greek word, *Philos* means friend and *Ateleia* means franchise.[1,2]

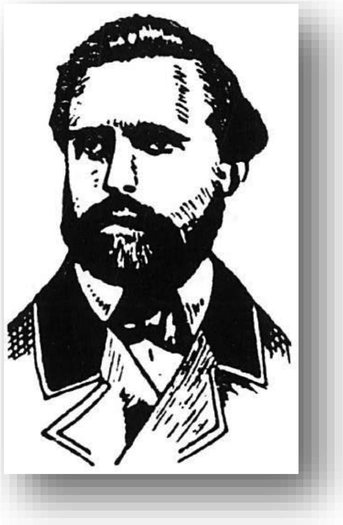

Figure 1.1.1.1 – *Herpin* (from ref. [1]).

A collection object is susceptible to forgery and postage stamps are no exception. As such, over time they have been falsified, being sometimes difficult to differentiate a true postage stamp from the forged.

In the philatelic field, four categories of falsifications can be considered:

Postal: when the intention is to defraud the state, obtaining illicit profits[2,4]; the first postage stamp forgery observed in Portugal was made in 1887, known as "*Pera de Satanás*" (figure 1.1.1.2), which could be distinguished itself from the true postage stamps by the imperfections in the impression and in the round jagged;

Figure 1.1.1.2 – The first Portuguese postage stamp forgery, *Pera de Satanás* (from ref. [5]).

Of war: the forgeries of postage stamps of other countries were carried out in war times; one example is the initiative taken by the British Secret Service to respond to the needs of its agents who were in Germany during the first World War;[2]

Propagandistic: used in times of war; the countries printed embarrassing postage stamps from the adversary countries, in order to offend their morality; frequently used during the second World War;[2]

Philatelic: are made to obtain easy and high profit, defrauding the philatelists, i.e., collectors. For example, ""*Hawaiian Missionary stamps are rare … an unused 2-cent stamp was sold in 1995 for $660,000*." (*sit in:* [6], p.A15); normally, these faked models are executed with high care and perfection.[2,4]

In view of the above, the analysis of postage stamps to determine their authenticity represents a clear demand for people involved in this field. Experts certified by the philately societies usually carry out this evaluation. However, the evaluations made are often merely visual, assessing in detail the design of the print, the jagged, etc. Although, additional questions can be added to the visual analysis of a postage stamp (which may be not of easy identification): e.g., what if the forgery is found in the ink? What is actually the chemical composition of the inks used to print the (true) postage stamps? If these are different in authentic and forged specimens, how can the authenticity of the former be validated? Many studies have been performed to fill this thematic gap and some of them will be described in the follow section – 1.4.

These questions are the bridge between the study of postage stamps and Forensic Chemistry, made in this work.

1.2 Portuguese Postage Stamp[1,3]

The organization of the Post Office in Portugal came with king D. Manuel I, on November 6th in 1520, when he established Luis Homem as “Correio-Mor”. Later, in the reign of D. Maria I, the State began to administer the Portuguese Post Office.

Portugal was no exception in the process how the mail was exchanged. The letters were charged according to their weight and distance to travel, and the associated fee was paid by the recipient. The sender could also pay this fee; this was, however, an unusual practice, known as frank postage or franchise.

From 1840 on, Portugal needed a reform that placed the country on the same level with the other nations, the global Postal Services. In 1851, the reorganization of the Postal Services was initiated, the conclusions of this commission were the base of the Law Decree of October 27th, 1852. This lead to the grounds of the new Portuguese Postal Reform, further stipulating the use of the postage stamp, started on the 1st of July of the following year. According to this, the services became governed by a Regulation approved by Law Decree of May 4th, 1853.

Francisco de Borja Freire (FBF), employee of the Portuguese Coin House, was assigned by the Portuguese king D. Fernando II to learn the office of printing the postage stamps which was already in use in England. This work involved to study the process of printing of the embossed postage stamps. Two British postage stamps were the inspiration on the type of bust and in the initials FBF placed in the base of the neck. For this, an authorization to buy a printing machine and inks for the first impressions was requested.

The story continues and on April 23th, 1853, a box of printing inks and two barrels of gum arrived to the Portuguese Coin House and on the 27th, of that same month, the stamping machine.

On May 1853, the printing of the postage stamps of 25 kings ("25 reis") began and on July 1rst, of that same year, the first Portuguese postage stamps of 5 and 25 kings were put into circulation (see figure 1.2.1).

Figure 1.2.1 – First Portuguese Postage Stamps, "5 e 25 reis" (5 and 25 kings).[7]

It is worth noting that, in which regards to the postage stamps, the counterfeiting is not a recent issue. Indeed, as earlier as 1879, this concern with postage stamp forgery existed. *Gaspar Knüschi* addressed a proposal to the Coin House in January 1879. He discovered a paint that could be used to expose falsification immediately (the ink was only applied to the postage stamps printed by him). This ink when applied to the "true" postage stamps induced a colour change in contrast to what happened with the forgeries, i.e., when the ink was applied no colour change could be observed in the "false" postage stamps. However, this proposal and method of forgery detection did not succeed.[1]

1.3 Dyes / Pigments

Since prehistoric times man used dyes and its use was recorded in grottos and caverns. Before going into further considerations, two concepts relative to dyes and pigments need to be clarified. These two concepts are differentiated by their solubility: *dyes* are usually organic compounds that are soluble in a solvent, while *pigments* are generally of inorganic origin and insoluble in most solvents, so they are dispersed in the matrix. There are however some exceptions; in these case dye behaves like a pigment, with low solubility and the pigment has a good solubility.[8,9]

Natural dyes, are those found in secretions of sea snail or in some insects. They were used, in ancient times, for example, to dye fibers or in paintings. *Lake pigments* have been used in paintings too. These lake pigments are formed by a precipitation through a complexation with a metal ion to achieve a better bounding with the fibers/textiles. Metal ions are normally designated as mordants, aluminium ion is a good example of a mordant. Dyes without mordant are known as vat dyes, indigo (the oldest natural dye[11]) is an example of these type of dyes, and the anthraquinones are an example of a group that can be used as a lake pigment. Their presence can be found in the ancient Egypt and in medieval illuminations.[8] Indeed, in the ancient Egyptian and Chinese civilizations, “synthetic” pigments like Egyptian Blue, Han Blue and Han Purple were known to be used.[10]

In Medieval times, Ultramarine, extracted from a *lapis-lazuli*, was used for religious paintings. In 1704, the synthesis of Prussian Blue establishes the beginning of the industry of synthetic pigments. The painters began to use it in their paintings, replacing the use of Ultramarine Blue. An example of this, is the work of Canaletto, where in its first works he used Ultramarine Blue and progressively moved to Prussian Blue.[12] This transition was also found in the engraved Japanese postage stamps (see next section).

For the green tones, mixtures of blue and yellow (lead-tin yellow) were used and for the reds vermillion/cinnabar (grinding it into powder from the mineral, HgS).[12,13] For the blues, besides the above mentioned (Ultramarine Blue and Prussian Blue), indigo was also used very often, due to its light stability and organic origin (from the *Indigofera* plant in ancient India).[8] The reds used in ancient times also had a natural origin; e.g. alizarin, and their derivatives (purpurin), Dragon Blood and Brazilwood. Alizarin (an anthraquinone) was obtained from the roots of some madder plants. Lacaic acid, kermesic acid and carminic acid (see figure 1.3.1) were another source of reds obtained from insects.[8]

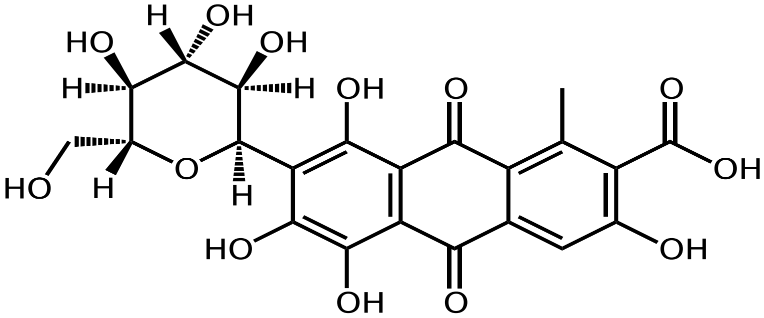

Figure 1.3.1 – The chemical structure of carminic acid.[8]

The ancient purple (Tyrian Purple), another natural dye, was obtained from the Mediterranean shellfish of the genera *Purpura: Murex brandaris*. This colour achieved the position of sacred colour and was a status symbol from the Roman Emperors.[8]

In 1856, mauveine was synthesized by *William Henry Perkin*, this was an important landmark in the history of science and technology since it is in the genesis of the synthetic dye industry. With this discovery, the use of ancient purple colour was reborn in the 19th century with the *mauvemania*. Queen Victoria used mauveine in her dresses and this beautiful colour was also used to dye some of the first postage stamps of the United Kingdom, it will be described in following section.[8,10]

The discovery of benzene structure due to *Kelulé* lead to the synthesis of new compounds. Driven by the knowledge of these structures, *Hofmann* synthesized aniline blue, a tryphenyl derivative from Rosaline, and showed that different alkyl groups could be introduced in the molecule producing dyes with many purple and violet colours – these later become known as the "Hofmann's Violet".[10]

In 1858, *Giess* discovered the diazo compounds, which gave rise to a large class of synthetic dyes - the azo dyes.[10] In 1859, fuchsine was synthesized by *Verguim*.[10,11]

In 1874, eosin (figure 1.3.2) was synthesized by *Caro*, due to the previous discovery of *Adolph von Baeyer*, in 1871, that from the reaction of phthalic anhydride with phenol fluorescein is produced, a molecule displaying a high fluorescence.[11]

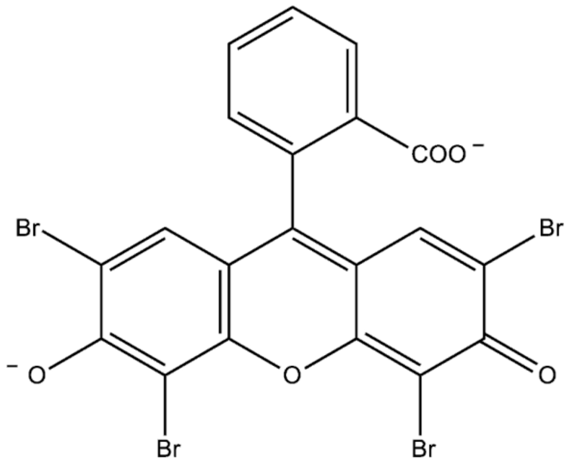

Figure 1.3.2 – Eosin y structure.

Postage stamps have been studied to determine the source of the printing material and to distinguish a potential forgery from the authentic specimen.

In the next section, a literature review of the molecules of colour that have been identified in postage stamps is.

1.4 State of the Art in Dyes and Pigments in Postage Stamps

Several studies have been carried out on postage stamps from several countries, such as, the rare Hawaiian Missionary stamps which were compared original, forgeries and reproductions[14], the 1847 1d orange–red Mauritian stamp, the 1847 2d deep blue unused stamp[15], some Brazilian stamps (printed between 1850 and 1922)[16] , the Chile first postage stamps[17], some Spanish (Spanish 15 cents stamp from the King Alfonso XIII (1889-1901))[18], the one-penny postage stamps between 1841 and 1880[19], a recent work on Japanese pioneer samples[20] and the most relevant include the iconic mauveine dye in UK 6d postage stamp from 1867-1880.[21]

Regarding the Hawaiian Missionary stamps, using the technique of Raman microscopy, the authors compared original postage stamps (1851-1852 AD) with forgeries and reproductions. The Hawaiian Missionary stamps are now included, over 160 years later, as the rarest and most valuable philatelic item. In this study, in the genuine postage stamps it was found that the ink used was Prussian blue, $Fe_4[Fe(CN)_6]_3{\cdot}14\text{–}16H_2O$, for the blue ink, and in this same blue ink, yellow particles of red lead, Pb_3O_4, were found. On the other hand, in the falsifications the ink consisted a mixture of Prussian blue with Ultramarine blue; or even more dramatically, it had been replaced by phthalocyanine blue, $CuC_{32}H_{16}N_8$, a modern synthetic pigment.[14]

Also, using Raman Microscopy, the original (1847) and the 1858–1862 counterfeit postage stamps of Mauritius were analyzed.[15] The rarity and hence the high value reached by these Mauritian stamps – with the rarest achieving about £1 million at an auction – lead to the forgery of this rare specimen. For the original 1847 1d stamp, the orange-red pigment was determined to be lead (II, IV) oxide (Pb_3O_4 - red lead); the original and reproduction 1847 2d stamps, differ in the shades of blue and in the paper fibber some crystals belonging to an ultramarine, have been detected. This made it possible to distinguish the reproduction (with the crystals) from the original specimen.[15]

Brazilian postage stamps were analyzed with an energy dispersive X-ray fluorescence (EDXRF) to understand the elemental profile of the ink. In this study, the ability of EDXRF to provide a characteristic profile of postage stamps was evaluated.[16] Authentic and counterfeit samples were investigated. From the EDXRF analysis, it was possible to characterize some inks, such as, red, which contain Hg and S from cinnabar or Fe and Si from a natural dye - a red ochre; the violet ink had S, Ca, Fe, Zn, Ba and Pb; the green pigments, associated to chromium oxides, with the detection of chromium; other inks were characterized, like brown and orange.[16] This analysis allowed distinguishing counterfeit and authentic postage stamps; these are further illustrated in figure 1.4.1 where authentic and forged postage stamps are depicted.

Figure 1.4.1 – An authentic (*Left*) and suspect of counterfeiting (*Right*) postage stamps. The area with a circle indicates the analyzed area (from ref. [16]).

These postage stamps were analyzed showed differences in the EDRXF spectra (figure 1.4.2); from both samples it can be observed that in the authentic postage stamp, Fe with a high intensity, Ba and Si were identified (characteristic from a natural red dye). On the other hand, the counterfeit sample is characterized by the absence of a signal for Ba and Si, as well as peak intensities changes for Fe.[16]

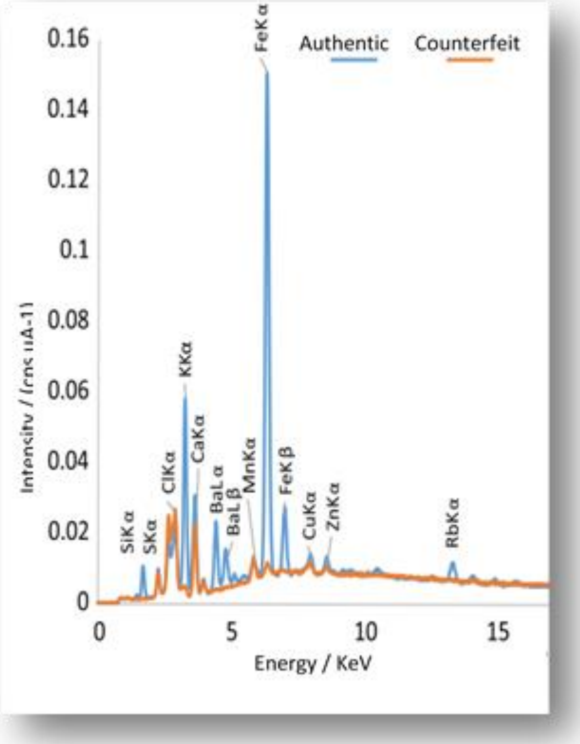

Figure 1.4.2 - Overlapped EDXRF spectrum of authentic and counterfeit stamps (from ref. [16]).

The first Chilean postage stamps (figure 1.4.3) covering the period between 1853 and 1862 were also subjected to chemical analysis. This study had four purposes: to analyze (i) the colour (by colourimetric and luminescence techniques), (ii) the paper (composition, sizing, thickness, and roughness), (iii) the ink and gum (pigment and binder composition) and (iv) the printing methods (engraving and lithography). The analysis performed provided an understanding of the characteristics of these postage stamps, showing that some techniques, such as X-Ray Fluorescence (XRF), Fourier Transform Infrared-Attenuated Total Reflectance spectroscopy (FTIR-ATR), colourimetry and X-Ray Diffraction (XRD), offer an effective, rapid, and nondestructive way of identifying the pigments and dyes of the inks.

Figure 1.4.3 – First Chilean postage stamps (from ref. [17]).

For the postage stamp identified as number #2 it was possible to conclude, from XRF mapping, that Fe and Pb are present in the ink (see figure 1.4.4). From FTIR-ATR analysis, calcite was identified in all postage stamps. In the red ink, cyanide bands, with peaks at 2080, 2060 and 2040 cm^{-1}, were observed. Lead chromate ($PbCrO_4$) were found to be present in the yellow and green inks, again by XRD.[17]

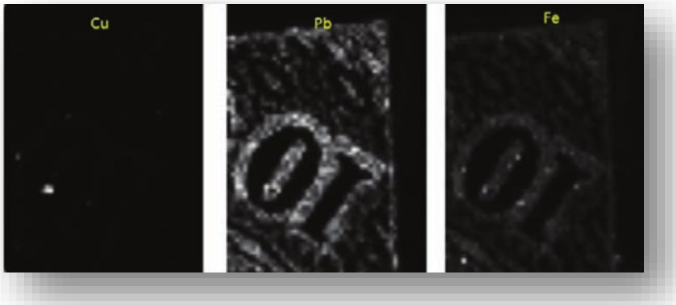

Figure 1.4.4 – XRF mapping of postage stamp 2 (from ref. [17]).

The King Alfonso XIII (1889 - 1901 ‘‘Pelón’’) 15 cents postage stamps, from Spain, were analyzed using non-invasive techniques: micro-Raman and micro-XRF. In these stamps, the 15 cents stamps are chestnut-brown. The aim of this study was to confirm the authenticity of these 15 cents postage stamps through the colour error; the reason of this colour error is the absence of carbon black. In a standard 15 cents stamps, XRF analysis detect the presence of iron, due to the use of an iron oxide in ink, and with Raman spectroscopy it was confirmed that, it is a mixture of a red iron oxide (hematite, Fe_2O_3) with a black amorphous carbon pigment, see figure 1.4.5 - a). In a colour error 15 cents stamps, the presence of iron was observed by XRF, confirmed by Raman analysis, a decrease of the signal of carbon black was observed, see figure 1.4.5 - b).[18]

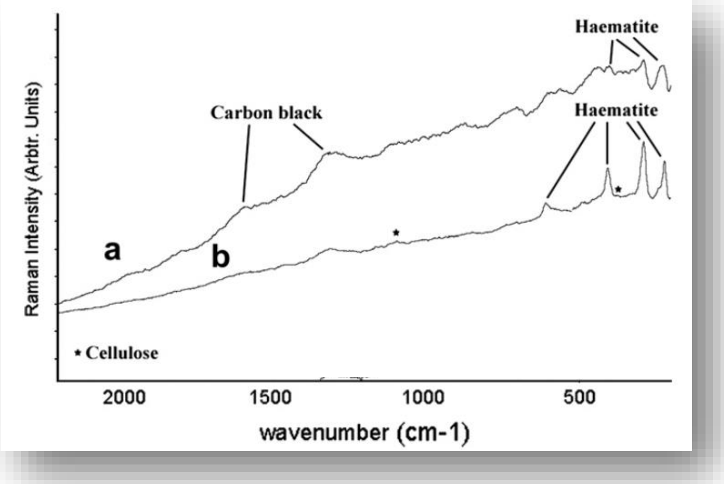

Figure 1.4.5 - Raman spectrum of (a) the ink obtained from standard 15 cents, (b) the ink obtained from colour error stamps (adapted from [18]).

The pioneer Japanese postage stamps, hand engraved, from 1871-1876 were analyzed (figure 1.4.6). In this study, one of the objectives was to distinguish stamps engraved by two different engravers, a private, *Atsutomo Matsuda* and, from 1873 on, by the Japanese Government, studying all colours used for printing the postage stamps. The analysis consisted in non-invasive techniques (FTIR, Raman, XRF and absorption spectroscopy), and invasive (HPLC) for the chemical analysis of the postage stamps.[20]

Figure 1.4.6 – Some examples of the Japanese postage stamps analyzed in ref. [20].

The origin of the different postage stamps colours, such as, blue, yellow, green, brown, purple and black were analyzed and it was concluded that *Matsuda* printing used mostly inorganic pigments like Prussian blue, vermilion, red lead, in contrast to the Government printings, which used Ultramarine blue, cochineal, chrome yellow, emerald green and triphenylmethane. It was therefore, hypothesized that *Thomas Antisell,* an American chemist, could have done this. Indeed, he was hired by the Japanese Government, in March 1872, to improve the printing inks. Table 1.4.1 summarizes the work on these postage stamps, namely the change of pigments over this time period, 1871-1876.[20]

Table 1.4.1 – Summary of the change of the pigments in postage stamps[a)] (from ref. [20]).

Year	Printer	Blue	Red	Yellow	Orange	Green	Brown	Purple	Black
1871	Matsuda	P	V, R			P, X	O, B		
1872		P	V, R			P, X	O, B R, B	X	B
1873	Government	P, U	C, R	Y		E			
1874		P, U	C, R	Y		P, Y	R, B	U, C	B
1875		U	C	Y	R, Y	P, Y	R, B	T	B
1876						E			

a) P: Prussian blue, U: Ultramarine, V: Vermilion, R: Red lead, C: Cochineal, Y: Chrome yellow, X: Unknown, E: Emerald green, O: Red ocher, B: Carbon black, T: Triphenylmethane dye.

A recent study of Queen Victoria's Lilac postage stamps showed that mauveine was used to dye these in the 1867-1880 period. HPLC-DAD-MS/MS, was used for chemical analysis and led to the identification of two postage stamps dyed with mauveine but from different synthetic methodologies (figure 1.4.7).

Figure 1.4.7 – Examples of postage stamps; at the *left,* dyed with Perkin's mauveine; at the *right* dyed with Caro's mauveine (adapted from ref. [21]).

The authors concluded, from more than 35 different lilac postage stamps, that mauveine was used for most of the 6d postage stamp from 1867-1880; a surprising result that, carminic acid (chochineal) was found as the main dye in some of the postage stamps (figure 1.4.8).[21]

Figure 1.4.8 - Two postage stamps with a similar lilac colour, but at *Left* had an extract of carminic acid and at the *Right* the mauve extract (adapted from [21]).

The previous literature review can be considered as an introduction to our study and to the main question that this study will attempt to respond: What were the dyes/pigments used in the first Portuguese Postage Stamps?

What is known regarding the first Portuguese postage stamps is that the dyeing stuff had its origins in a box that came from London. The constitution of the inks (namely in this box) remains unknown till our days.

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Chapter II

Experimental Methods

2.1 X-Ray Fluorescence (XRF)

X-ray Fluorescence is a powerful technique in forensic analysis being able to be applied to a variety of different materials providing a qualitative and quantitative assessment. Moreover, XRF does not demand a sample pre-preparation and is a non-destructive technique.[1,2]

This technique uses X-rays to excite electrons from the electronic levels (orbitals) of the atomic structure causing the emission of characteristic photons (fluorescence) when the atom returns to its ground state. The emitted photons correspond to the atomic energy levels, which are characteristic of a material.[3] The energy levels are counted from nucleus to outer levels, initiating with K (1) until the last level, P, being the K level the most energetic and the outer the less energetic. This process is depicted in the figure 2.1.1.[1,2]

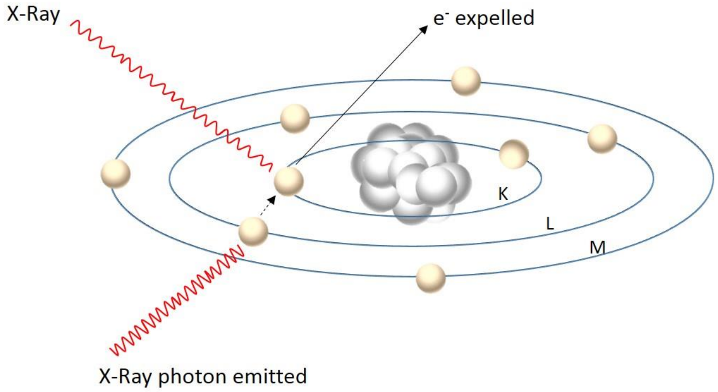

Figure 2.1.1 – Schematic representation of the process that occurs in XRF technique.

The atom fluorescence is characteristic of inner shell transitions and is labelled through the Greek letter (α, β, γ), relating the orbital level (K, L, M…) where a hole was produced, e.g., if the electron was in the L level and filled up the orbital K, this is called Kα.[1,2]

The equipment consists of a source, support for sample, the detector and the software analyses, see figure 2.1.2.

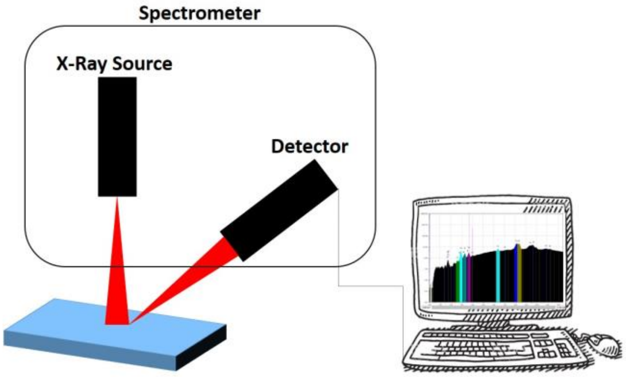

Figure 2.1.2 – Schematic representation of XRF analysis.

Acquisition:

The analysis was performed with a Hitachi X-Ray Fluorescence model EA6000VX. For the elementary analysis the measurement conditions were 60 seconds, collimator with 1.2x1.2 mm, current at 1000 µA, and voltages at 15 kV (measurement without filter) and 50 kV (filter for Pb). For the mapping of some elements the conditions were 60µm/pixel, 50.00ms per pixel, collimator with 0.2x0.2 mm, current 1000 µA. For some elements it was used voltage at 15 kV, some of them with filter for Cr, and voltage at 50 kV, some analysis with filter for Pb.

2.2 Photophysical Techniques

In this chapter a brief description of photophysical processes which may occur in these molecules (dyes and pigments) will be presented.

When radiation reaches a sample three things may happen: transmission, reflection or absorption. The absorption occurs when the radiation is taken by the medium. The absorption of visible light is the reason for some molecules have colour and colourants (dyes)/pigments is no exception.[5,6]

The absorption of ultra-violet (UV) and visible (Vis) radiation induces an electron to a higher energy level, an excited state (S_n). The molecule the returns to a fundamental state (or, normally named, ground state, S_0).

This deactivation to the ground state can be made through three different ways: radiationless transitions (internal conversion or intersystem crossing), emission of radiation (fluorescence and phosphorescence) and, finally, photochemical reactions (degradation). [5,7] These can happen individually or combined.[7] Some of these phenomena are represented by the well-known *Jablonski Diagram*, see figure 2.2.1.[5]

Internal conversion is a non-radiative process that occurs between two states with same spin multiplicity; intersystem crossing occurs between two states, but with different spin multiplicity and is also a non-radiative process. Phosphorescence happens when the light is emitted due to the transitions that involves two states of different spin multiplicity, i.e., from vibrational relaxed triplet state (T_1) to the ground state (S_0); fluorescence is when light is emitted due a transition of the type $S_1 \rightarrow S_0$, from a singlet lower energy state to the ground state, i.e., between two states with same spin multiplicity.[5,7]

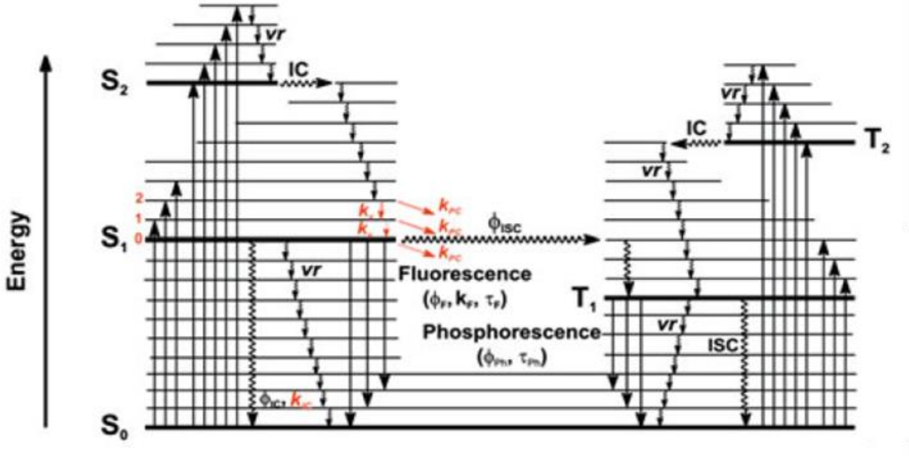

Figure 2.2.1 – A typical *Jablonski-Perrin* diagram representing all the possible photophysical processes that may occur in a molecule upon excitation (adapted from ref. [8]).

The condition necessary to have an electronic transition from the ground state to an excited state is that the photon need to have energy which match the gap between these two states.[7]

The absorbance (A) of each wavelength, by the sample, is reflected by the Beer-Lambert law, given by the formula

$$A = \varepsilon l c \qquad (2.2.1)$$

where ε is the extinction coefficient at that wavelength, *l* is the path length, *c* is the dye concentration (in this case) and *A* is the absorbance of the sample. Being that, the absorbance is directly proportional to the dye concentration with a proportionality constant, ε.

Important parameters related to the fluorescence are its lifetime (τ_F) and the quantum yield (ϕ_F).[5,7]

The following subsections present the experimental conditions used to obtain the absorption and fluorescence emission spectra, together with the lifetimes and quantum yields of the dyes found in the postage stamps analyzed.

2.2.1 - UV-Vis Absorption

The solid state UV-Vis absorption spectra of the postage stamps and of the standards (carminic acid, vermillion, hematite, eosin y, fuchsine, lead chromate, lead oxide, lead sulfide) were obtained by diffuse reflectance using a Cary 5000 UV-Vis-NIR spectrophotometer equipped with an integrating sphere in the reflecting mode. For the standards were obtained in the solid (powder) and gouache (the standard powder was dissolved in water and potato starch and after was painted on filter paper) forms. Before the spectra of postage stamps and solid standards were recorded, a baseline, with barium sulphate, was obtained. For the gouache samples, the baseline was acquired with filter paper.

2.2.2 – Fluorescence Emission Spectra

Fluorescence Emission spectrums were measured in Fluoromax – 4 Spectrofluorometer Horiba Scientific, using the FluorEssence V3.5 software. The liquid samples were collected having the same absorbance, the postage stamp and the standard (eosin y).

2.2.3 - Time-Resolved Fluorescence Measurements

Fluorescence decays were measured using a home-built picosecond time correlated single photon counting, TCSPC, apparatus (3 ps time resolution) described elsewhere.[8] The fluorescence decays and the instrumental response function (IRF) were collected using a time scale of 1024 channels, scale of 16.3 ps/ch, until 5×10^3 counts at maximum were reached. The excitation source consisted on a PicoLED (λ_{exc}= 451 nm) from PicoQuant. For the solution sample of eosin y emission wavelength was collected at 560 nm whereas in the solid postage stamps and dyed paper, the emission wavelength was collected at 600 nm. Deconvolution of the fluorescence decay curves was performed using the modulating function method, as implemented by G. Striker in the SAND program.[9]

2.2.4 - Quantum Yields

The fluorescence quantum yields (ϕ_F) for eosin y in the solid state and in postage stamps was obtained by the absolute method using a Hamamatsu absolute PL quantum yield spectrometer Quantaurus C11347 (integrating sphere), with an excitation wavelength at 450nm.

2.3 High-Performance Liquid Chromatography (HPLC)[10–12]

High Performance (or Pressure) Liquid Chromatography (HPLC) is a technique which allows to separate different compounds in a mixture, providing a qualitative and a quantitative information.

In this technique, the sample flow into a mobile phase (liquid) that pass through a stationary phase by a pump (at elevated pressure). This stationary phase is a column packed with small porous particles. When the mixture passes through the column, molecules can be retained for a more or lower time, depending on their affinity for the column. The compound with more affinity for stationary phase will stay for much longer time attached to the column while the compound with less affinity will take less time to run all the length of the column and be detected.

These differences in the interaction between the compound and the particles in the column will be represented by a chromatogram that shows the elution at different times, normally designated retention time. The chromatogram is not enough to have a positive identification because some different compounds can be eluted from the column at the same time and chromatograms will be the same. Taking this into account, several detectors can be coupled to this technique, like the UV-Vis absorption, refractive index, fluorescence, electrochemical and mass spectrometry.

In this work, two different detectors - Mass Spectrometry (MS) and the UV-Vis absorption - were used. The first one provides information about molecular mass, allowing predicting some structural characteristics, its composition and, when possible, their isotopic proportions. This technique gives a fragmentation pattern with a ratio of m/z, mass vs. charge, which is characteristic of each molecule.

Finally, the *Diode Array Detector* (DAD) is the most commonly used to analyze organic compounds and in variable wavelength. This detector performs a spectroscopic scanning to determine the absorbance at a several wavelengths (very useful when it is unknown the absorption wavelength of the compounds) while the sample pass through the flow cell.

In the next subsections the experimental conditions used to perform the HPLC-MS and HPLC-DAD analysis of the postage stamps are mentioned.

2.3.1 - Postage Stamps Extraction

The procedure used in this work reproduce what was made in *Conceição Oliveira, M.*[14], with a small changes. A few piece of a postage stamp was extracted with a 200 µL solution of 0,2 M oxalic acid/methanol/acetone/H_2O (1:3:3:4, v/v/v/v) in 1,5 mL Eppendorf at the 60 ^oC in a water bath with constant stirring until the paper loses their colour (which took approximately 30min). After extraction, the samples were dried in a nitrogen line under heating with a dryer, the residues were reconstituted in 50 µL MeOH, ultra sounds and 50 µL H_2O before to do the HPLC-MS and HPLC-DAD analysis.

2.3.2 - HPLC-MS

The postage stamps extractions were analysed in a DioneX UltiMate 3000 Pump-Thermo Scientific using a TOF Kinetex C18 column (2,1 mmx150 mm, 1,7 µm, 100 A). A solvent gradient with acetonitrile (A) and acid water (formic acid, 0,1% v/v) (B), was used in different proportions of A and B: 0min - 5% A/95% B; 1,5min - 15% A/85% B; 8min - 50% A/50% B; 10min - 70% A/30% B; 18min - 100% A; 28min - 5% A/95% B; 30min - 5% A/95% B; with a flow rate of 0,150 mL/min at the 35 ^oC, and the chromatograms were obtained by LC-HRMS/ESI (-).

2.3.3 - HPLC-DAD

The extracted dyes from the postage stamps were analysed in an Elite Lachrom HPLC-DAD system with L-2455 Diode Array Detector, L-23000 Column Oven (RP-18 endcapped column), L-2130 Pump and a L-2200 Auto Sampler. A solvent gradient was performed with acetonitrile (A) and acid water (formic acid, 0,1% v/v) (B), was used in different proportions of A and B: 0min - 5% A/95% B; 1,5min - 15% A/85% B; 8min - 50% A/50% B; 10min - 70%

A/30% B; 18min - 100% A; 28min - 5% A/95% B; 30min - 5% A/95% B, with a flow rate of 1,5 mL/min at the 35 ^{o}C. The HPLC-DAD chromatograms were acquired at 460 nm and 524 nm.

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Chapter III

Results and Discussion

Eighteen groups (each with 1-3 replicas) of Portuguese postage stamps with red, pink and purple colours were analysed. A total of forty-nine postage stamps (including replicas) were investigated. The identification (with the acronym) of all samples is based on their catalogue number (13-160), the production year (1857 to 1909) and replica number (1-3); for instance, the acronym 13_1857-62_Rep1 reflects the postage stamp with a catalogue number of 13, produced between the years of 1857-1862 and is the replica #1. The postage stamps were characterized by XRF, photophysical techniques (UV-Vis absorption, Fluorescence Emission, Time-Resolved Measurements) and HPLC-MS/HPLC-DAD.

3.1 XRF Analysis

An initial analysis intended to differentiate between the organic or inorganic origin of the molecules of colour present in the postage stamps. With this in mind, the results were collected from the inked area and the back of the stamp (for now on, named as “paper”), to minimize the ink contribution (see figure 3.1.1 as an illustrative example).

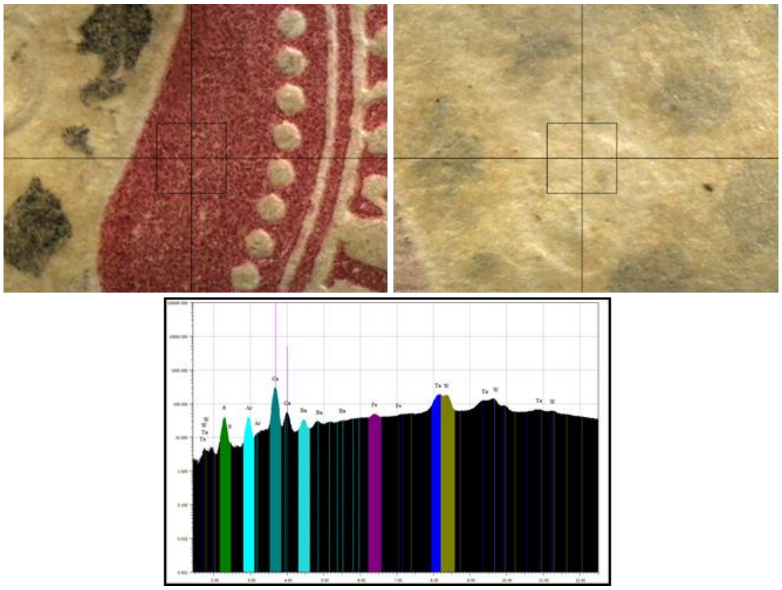

Figure 3.1.1 – Example of the XRF analysis on 30_1867_Rep1 postage stamp. Acquisition conditions: current at 1000 µA, collimator at 1.2x1.2mm, voltage at 15kV, filter off, measurement time 60 seconds; XRF spectrum is cps vs energy, i.e., counts per second of photons vs their energy.

Data analysis was performed by doing a subtraction between the two spectra, i.e., the paper spectrum was subtracted from the ink spectrum.[1] Data is summarized in Table A1. In this work, it was possible to differentiate the organic and inorganic origin of the colouring materials in the postage stamps inks.

The organic dyes could not be identified by XRF[2,3] and they will be discussed in the next sections. The inorganic pigments, mercury (Hg), sulphur (S), lead (Pb), etc., were identified (see Table A1). The identification of these metal ions, was followed by a mapping (distribution) in the postage stamps. The mapping allowed to obtain the spatial distribution of each one of these elements. For an illustrative example of the mapping of Hg and Br, see figure 3.1.2.

Figure 3.1.2 – Mapping of (**A**) 22_1866_Rep1 and (**B**) 66_1884_Rep2 postage stamps for Hg and Br, respectively. Acquisition conditions: current at 1000 µA; collimator at 0.2x0.2mm; pixel size 60 µm/pixel; time per pixel 50,00 ms; voltage at 50kV; filter: for Hg: without filter, for Br: filter for Pb.

As others authors have also described[4,5], the simultaneous presence of Hg and S is an indication of cinnabar (HgS). From figure 3.1.2 **A**, it is shown that the Hg is present only in the red part of the postage stamp indicating that the pigment is indeed HgS. In the case of the bromine mapping the presence of an organic dye is suggested.

In the 30_1867_Rep1 and 30_1867_Rep3, HgS was also found, confirmed by the mapping for Hg (see figure 3.1.3) and the presence of S (Table A1), but, for 30_1867_Rep3, unexpectedly a different composition was obtained which will be discussed further on.

Figure 3.1.3 – Mapping of (**A**) 30_1867_Rep1 and (**B**) 30_1867_Rep3 postage stamps for Hg. Acquisition conditions: current at 1000 µA; collimator at 0.2x0.2mm; pixel size 60 µm/pixel; time per pixel 50,00 ms; voltage at 50kV; filter: for Hg.

For the 150_1898 postage stamps, the pigment found was lead oxide. The XRF analysis showed the absence of other metal ions and the mapping of Pb further confirm the presence of lead in the coloured part, as is illustrated in figure 3.1.4.

Figure 3.1.4 – Mapping of 150_1898_Rep2 postage stamp for Pb. Acquisition conditions: current at 1000 μA; collimator at 0.2x0.2mm; pixel size 70 μm/pixel; time per pixel 50,00 ms; voltage at 50kV; filter: for Pb.

Pb was also found in other postage stamps, such as 25_1867, 54_1880 and 149_1898 (see figure A1.1). The presence of this ion in the inked area, together with other ions show that, in 25_1867_Rep1 and 54_1880_Rep3 the dye is lead oxide (Pb_3O_4/PbO) or lead sulfide (PbS), for 25_1867, due to the presence of S (albeit in this case the mapping of S was not so conclusive). Once more, from previous works[4,5], the presence of Pb and chromium (Cr) is an evidence of the inorganic pigment, lead chromate ($PbCrO_4$). For the 149_1898 postage stamps, the XRF analysis detected the presence of Pb and Cr which is indicative of the presence of lead chromate, showed by mapping of Pb and Cr metals, see figure A1.1. The absence of the sulphate ion (see Table A1) likely indicates that it is this pigment present on postage stamp instead of the sulphate chromate, $PbCr_{1-x}S_xO_4$. [6]

Literature reports that the presence of some elements, such as Ti or Ba, is a proof of a natural origin, from mined source[2], and in a few postage stamps (25_1867 and 150_1898) these elements were also detected. This evidence supports even more that the pigment is from natural origin.

For the remaining samples, 13_1857-62, 16_1862-66, 22_1866_Rep1 and replica 2, 30_1867_Rep2, 40_1870-79, 62_1887, 63_1887-90_LR, 63_1887-90_VA, 66_1884, 130_1895, 141_1899, 156_1909 and 160_1909 postage stamps the dye found has an organic origin due to the absence of metal elements. The structure of these will be discussed in the next sections (section 3.2 – 3.5). For the 69_1892-94 sample, the analysis was inconclusive.

As (arsenium) was detected in the elemental analysis, but the mapping was not conclusive, i.e., this element is found dispersed in all over the postage stamp (see figure A1.2). In the majority of the postage stamps dyed with organic dyes aluminium was not found. This suggests that these dyes are not lake dyes.[7] In all of the postage stamps, S, iron (Fe), copper (Cu), calcium (Ca) and zinc (Zn) were found; Fe, Cu, and Zn are related with impurities from manufacture process, Ca would be related to the presence of fillers (like calcium carbonate) in paper and S due to the paper manufacturing.[1,5]

3.2 UV-Vis Absorption Analysis

After the analysis of the inorganic pigments present in the postage stamps, the work continued with the analysis of the organic dyes. This was initially done using UV-Vis spectroscopy.

A mixture of the dye with potato starch and water was made and painted over a filter paper, aiming to mimetic a similar matrix to that found for the dye in the postage stamps (see figure 3.2.1). The UV-Vis spectra of the postage stamps was obtained and compared with theses mixtures, from now on designated as *standard(s)*.

Figure 3.2.1 – Standards that was made to mimetic the conditions of postage stamps. Carminic acid, fuchsine and eosin y, from left to right.

The absorption spectra of the postage stamps were acquired in the high coloured area of the postage stamp and, when possible, avoiding the postmark. The absorption spectra of the *standard*s were obtained in their solid form (powder) and in the mixture (starch potato, water and the dye).

It was possible to determine the absorption spectra of each *standard* and compared to the postage stamps. Taking one postage stamp as an example (see figure 3.2.2), a good overlap between the postage stamp and the *standard*, in the visible region, can be observed. The lack of overlap in the UV region is due the cut-off of the paper.

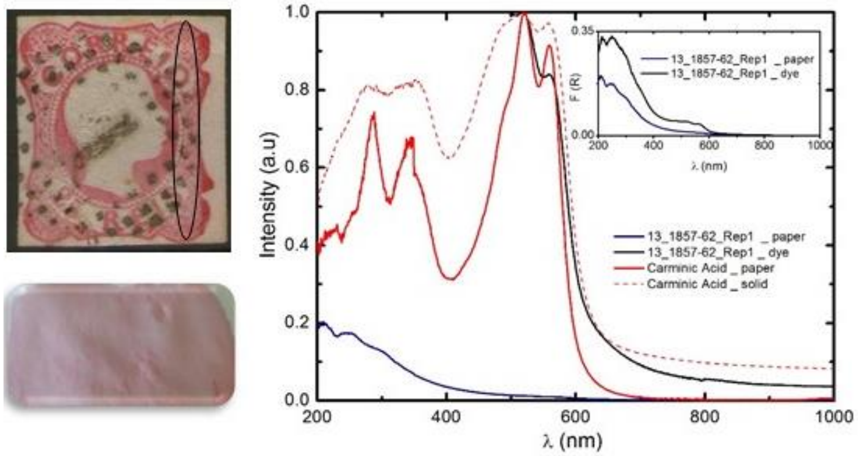

Figure 3.2.2- Absorption spectra comparing the 13_1857-62_Rep1 postage stamp – *paper*: back of the stamp; *dye*: coloured area (shown in the image by a circle) – with a *standard*, carminic acid – *paper*: filter paper painted with the standard; *solid*: standard in the powder form.

As can be seen in figure 3.2.2, the results suggest that carminic acid is the dye used in the postage stamps analysed. The replicas have the same result (see figure A2.1). Other groups of postage stamps have similar results suggesting the presence of this organic dye, as can be seen in figure A2.2. In addition, the dye in these postage stamps was extracted and analysed by HPLC-MS (section 3.3.1).

Taking into account, the study developed by *El Bakkaliet al.* [6], the carminic acid spectra shows a band with two well defined shoulders at 525 and 561 nm. In this work, these characteristic shoulders were obtained with a small shift, with maxima at 521 and 559 nm. The spectral data are summarized in Table 3.2.1.

As mentioned before, in section 3.1, the 30_1867_Rep3 sample showed a different pattern of the molecules of colour present, when compared with the other replicas. Indeed, despite the detection of Hg and S (that suggest the presence of cinnabar), from the absorption spectra, carminic acid is likely to be present too, see figure 3.2.3.

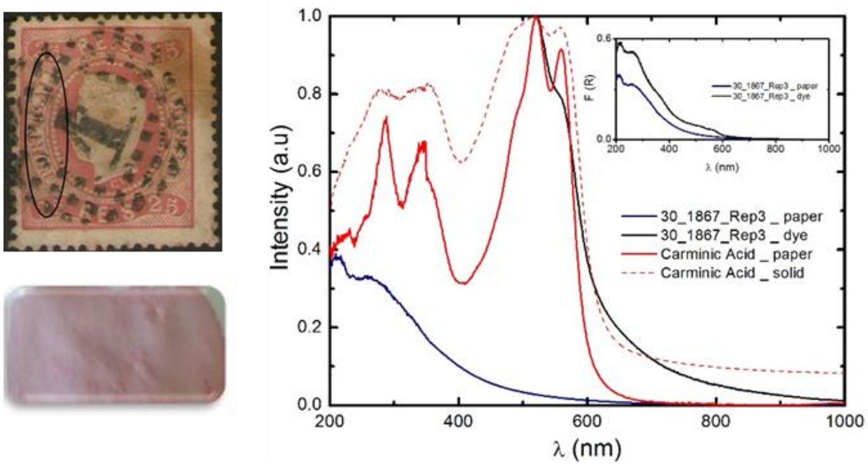

Figure 3.2.3- Absorption spectra comparing the 30_1867_Rep3 postage stamp – *paper*: back of the stamp; *dye*: coloured area (shown in the image by a circle) – with a *standard*, carminic acid – *paper*: filter paper painted with the standard; *solid*: standard in the powder form.

This lead to the question: why, were the dyes/pigments dyes in some of the specimens? This doubt raises the need to verify the presence of the organic dye, carminic acid, with HPLC (see section 3.3.2).

In 66_1884, 62_1887 and 160_1909 postage stamps, the suspicious dyes were eosin y and fuchsine due to their pink colour. As can be seen in figure 3.2.4, in the 66_1884_Rep2 postage stamp a perfect match with an eosin y in the visible region of the spectra (figure 3.2.4 **A**) is obtained; however, despite the shift between the postage stamp and fuchsine spectra some similarities can be noticed (figure 3.2.4 **B**). Again, in the UV region the lack of overlap is due to the cut-off of the paper. In order to clarify which dye is present, an HPLC analysis was performed (section 3.3.2).

With the 62_1887 postage stamps the different replicas showed a good overlap of the postage stamp spectra with the eosin y in visible region; for an illustrative example, see figure 3.2.5 and the remaining replicas are in figure A2.3.

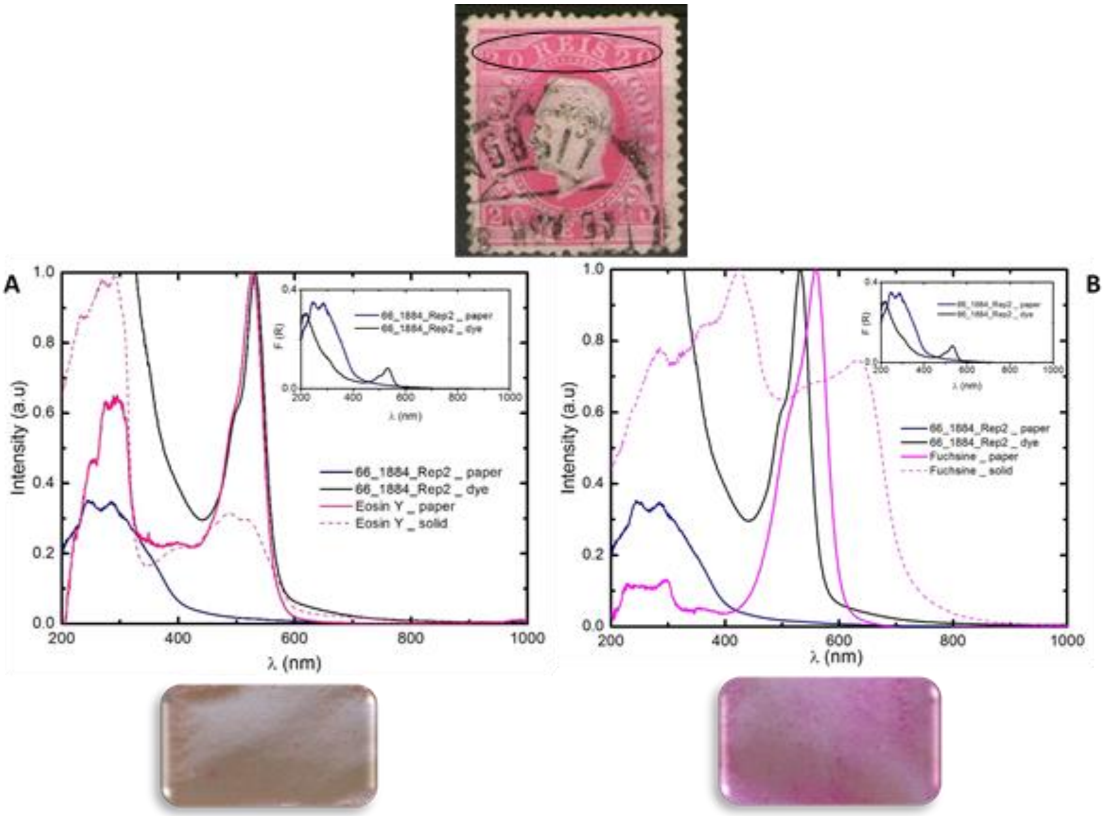

Figure 3.2.4- Absorption spectra comparing the 66_1884_Rep2 postage stamp – *paper*: back of the stamp; *dye*: coloured area (shown in the image by a circle) – with a *standard*, (**A**) eosin Y and (**B**) fuchsine – *paper*: filter paper painted with the standard; *solid*: standard in the powder form.

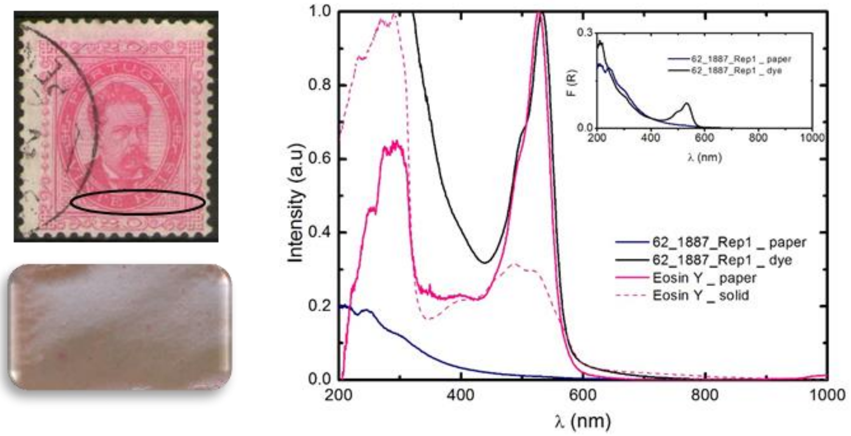

Figure 3.2.5- Absorption spectra comparing the 62_1887_Rep1 postage stamp – *paper*: back of the stamp; *dye*: coloured area (shown in the image by a circle) – with a *standard*, eosin Y – *paper*: filter paper painted with the standard; *solid*: standard in the powder form.

The 160_1909 postage stamps are no exception to the presence of eosin y as the colouring material (see figure A2.5). In the 160_1909_Rep3, the paper absorption spectra of the postage stamp, i.e., the back of the postage stamp, shows a band in the visible region coinciding with the band present in the ink. This is likely due to the high amount of dye in the "front" of the stamp and, due to its thickness, is also found in the back of the postage stamp.

For the 141_1899 postage stamps, despite their colour is more red than pink (or purple), the elementary analysis (by XRF) showed the presence of Br in the coloured area. Therefore, eosin y was used to do the comparison. In figure 3.2.6, the UV-Vis absorption analysis for 141_1899_Rep3 postage stamp are shown.

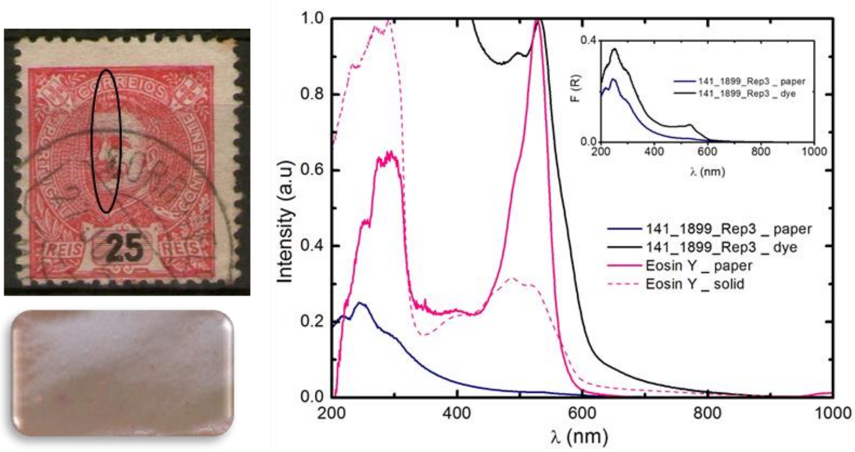

Figure 3.2.6- Absorption spectra comparing the 141_1899_Rep3 postage stamp – *paper*: back of the stamp; *dye*: coloured area (shown in the image by a circle) – with a *standard*, eosin Y – *paper*: filter paper painted with the standard; *solid*: standard in the powder form.

In contrast to what was expected, the absorption spectra did not show a good match with eosin y. In order to verify if the dye present was indeed eosin y, extraction of the dye followed by HPLC analysis was performed (see section 3.3.2).

The analysis of the remain 63_1887-90_LR, 63_1887-90_VA, 130_1895 and 156_1909 postage stamps was not so conclusive. Indeed, the 63_1887-90_LR has one band in the visible region but did not overlap with any of the standards (eosin y and carminic acid), see figure A2.4. The 130_1895 postage stamps display a naked eye shaded-purple colour. For the 156_1909 postage stamps, a beautiful purple colour is observed.

From Table 3.2.1, it can be seen that, for the postage stamps with, supposedly, carminic acid, the wavelength maxima vary between 516 – 523 nm; for the postage stamps with eosin y the wavelength maxima are in 529 – 533 nm range. Comparing with the standards, for carminic acid the maximum is at 521 nm and for eosin y at 527 nm, the wavelength can be considered identical, taking into account the heterogeneity of the media of a postage stamp.

Table 3.2.1- Absorption maxima for the different Portuguese postage stamps (and replicas) and *standards*, carminic acid and eosin y, investigated.

Postage Stamp		**λ $_{max}$ (nm)**
		Absorption
13_1857-62	Rep1	519
	Rep2	521
	Rep3	520
16_1862-66	Rep1	520
	Rep2	520
	Rep3	516
22_1866	Rep1	–
	Rep2	521
	Rep3	520
30_1867	Rep1	–
	Rep2	518
	Rep3	523
62_1887	Rep1	533
	Rep2	533
	Rep3	532
66_1884	Rep1	532
	Rep2	531
141_1899	Rep1	–
	Rep2	–
	Rep3	532
160_1909	Rep1	529
	Rep2	530
	Rep3	531
Carminic acid		521
Eosin y		527

3.3 HPLC Analysis

This section will be divided into two subsections – 3.3.1 and 3.3.2. In the first subsection will be presented the results from HPLC-MS and in the second section the results from the HPLC-DAD analysis.

3.3.1 HPLC-MS

For the HPLC-MS, the samples analysed were the 13_1857-62, 16_1862-66, 22_1866_Rep2 and Rep3, 30_1867_Rep2 and 40_1870-79 postage stamps. For each postage stamp a small piece was cut and the dye was extracted with the solution mentioned in the section 2.3.1 (HPLC – Postage Stamps Extraction). The carminic acid was used as *standard* and compared with the postage stamps.

The chromatogram and the mass spectrum of the *standard* are shown in figure 3.3.1.1.

The HPLC results of 13_1857-62_Rep1, 16_1862-66_Rep1, 22_1866_Rep2 and 40_1870-79_Rep1 postage stamps are shown in figure 3.3.1.2 to figure 3.3.1.5. The remaining postage stamps HPLC results are presented in the figures A3.1 – A3.4.

An early study made by *Conceição Oliveira, M.*[8], found carminic acid in the postage stamps analysed. The retention time obtained, in their conditions, for carminic acid was at 11 minutes and the m/z was 491 for this deprotonated molecule.

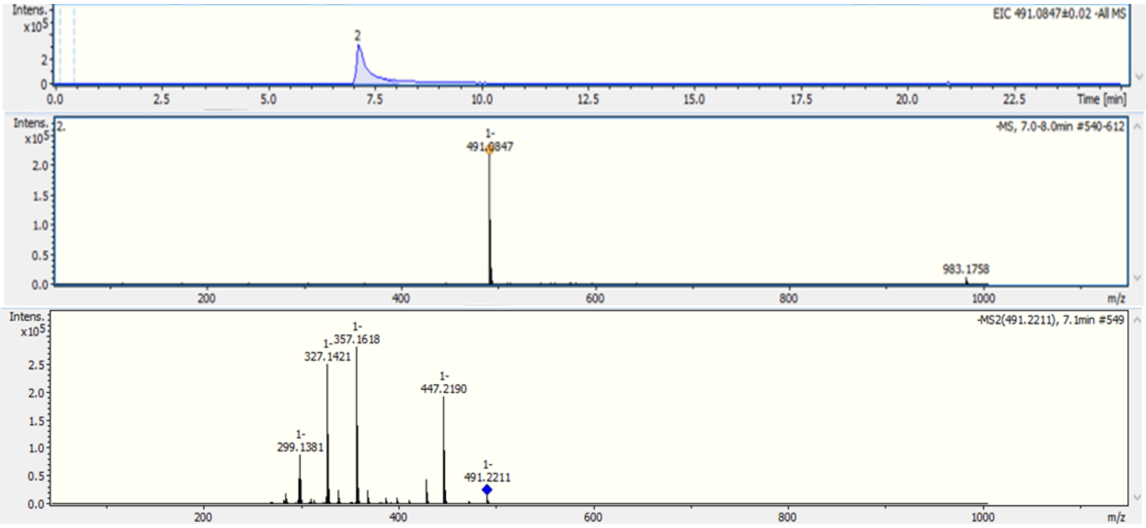

Figure 3.3.1.1– The extracted ion chromatogram for the ion m/z 491 (deprotonated carminic acid molecule). Spectra ESI (-)/MS plotted to the top of peak 2 and the MS-spectra of [M-H]$^-$ m/z 491.

In this figure, the chromatogram of carminic acid is presented with a single peak at 7.25 minutes. The mass spectrum of this peak shows the mass of the ion, at m/z 491 (corresponds to the deprotonated carminic acid), and is displayed the fragmentation pattern.[9]

The results were quite similar to those of *Conceição Oliveira, M.*[8] , except in the retention time value. The slightly difference obtained in different studies for the retention time is quite usual due to the different experimental conditions.

In figures 3.3.1.2 to 3.3.1.5 the HPLC chromatograms of the extracts of the postage stamps 13_1857-62_Rep1, 16_1862-66_Rep1, 22_1866_Rep2 and 40_1870-79_Rep1, respectively, are shown.

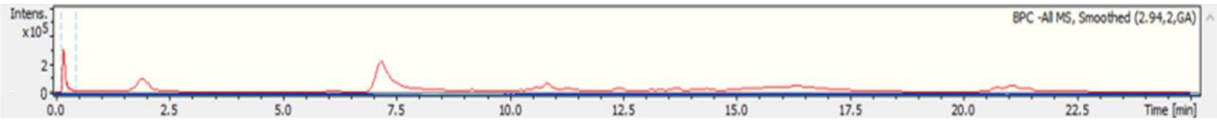

Figure 3.3.1.2– Total ion chromatogram obtained by LC-HRMS/ESI (-) for the 13_1857-62_Rep1.

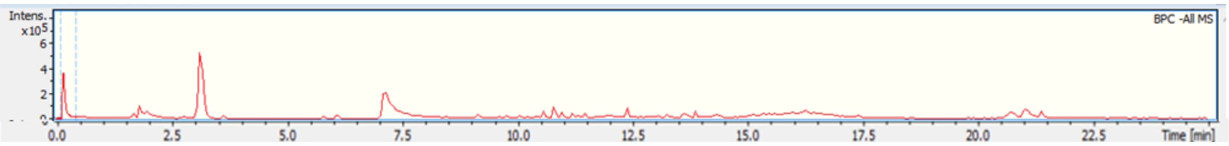

Figure 3.3.1.3– Total ion chromatogram obtained by LC-HRMS/ESI (-) for the 16_1862-66_Rep1.

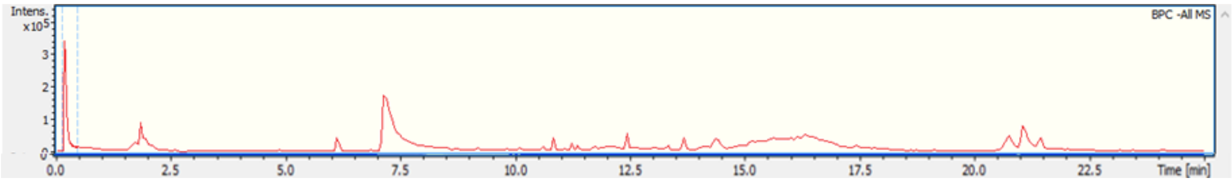

Figure 3.3.1.4– Total ion chromatogram obtained by LC-HRMS/ESI (-) for the 22_1866_Rep2.

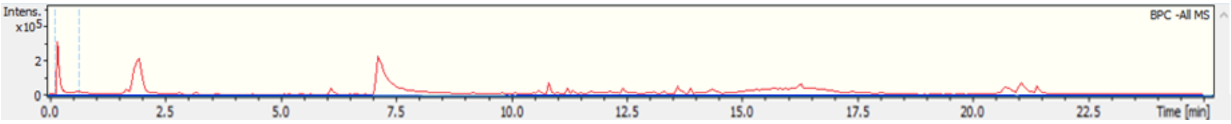

Figure 3.3.1.5– Total ion chromatogram obtained by LC-HRMS/ESI (-) for the 40_1870-79_Rep1.

From figures 3.3.1.2 – 3.3.1.5 it can be seen that the peak corresponding to the carminic acid is present in all, at the same retention time (approximately at 7.25 minutes). The intensities of the peak vary which is related to the different amount of the dye present in the extract (higher or lower dye concentration in solution). Other residual peaks are present in addition to the carminic acid peak. They can be related to vestiges of the synthesis procedure or from the extraction process and/or the solvents used. The other replicas showed identical results (see figures A3.1 – A3.4).

In Table 3.3.1.1 are present the retention times of the postage stamps and the *standard,* carminic acid.

Table 3.3.1.1- Retention times (obtained from HPLC-MS) of postage stamps and the *standard*, carminic acid.

Postage Stamp		**t_r (min)**
13_1857-62	Rep1	7.25
	Rep2	
	Rep3	
16_1862-66	Rep1	7.25
	Rep2	
	Rep3	
22_1866	Rep2	7.25
	Rep3	

30_1867	Rep2	7.25
40_1870-79	Rep1	7.25
	Rep2	
	Rep3	
Carminic acid		7.25

3.3.2 HPLC-DAD

The postage stamps analysed by HPLC-DAD were 30_1867_Rep3 (because its unexpected result obtained from the UV-Vis absorption analysis), 66_1884_Rep2 (as mentioned in the section 3.2, was not clear which dye is present, eosin y or fuchsine) and 141_1899_Rep3 (with eosin y as the questioned dye). A small piece of the postage stamp was cut and the dye extracted as mentioned in section 2.3.1 (HPLC – Postage Stamps extraction), as was done in the HPLC-MS analysis. The *standards* used were carminic acid and eosin y.

In *Balakina, G. G.*[10], the carminic acid is reported to have an absorption spectra with three wavelength maxima: 274, 312 and 495 nm. In our study, a peak at approximately 495 nm was observed in the visible region.

In figure 3.3.2.1 it can be seen that the major compound present in this postage stamp, 30_1867_Rep3, is carminic acid. The chromatograms display a small difference (0.33) in the retention time values but the absorption spectra show a good overlap, confirming that carminic acid is present in the postage stamp.

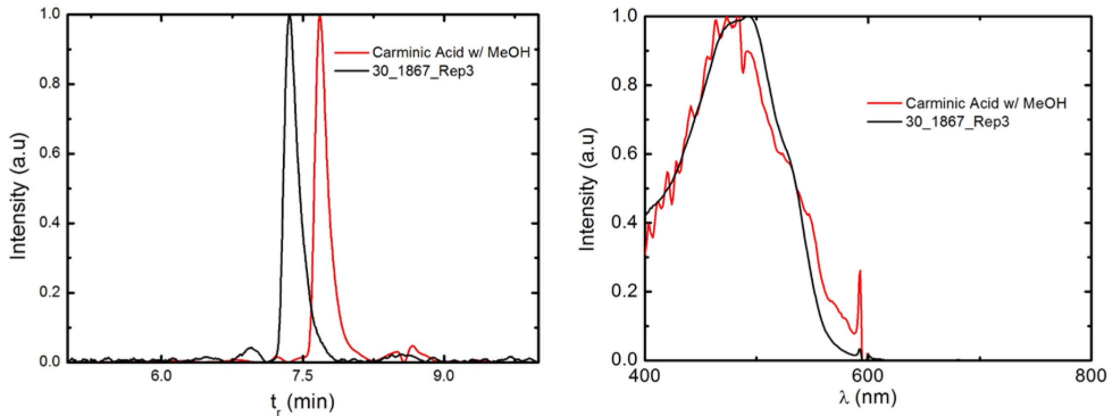

Figure 3.3.2.1- HPLC chromatograms and absorption spectra of the 30_1867_Rep3 postage stamp extract and of the standard, carminic acid.

Regarding eosin Y, in *Chakraborty, M.*[11], the absorption spectra was found with maxima at 496 and 517 nm.

For the 66_1884_Rep2 postage stamp, the HPLC-DAD results are shown in figure 3.3.2.2. It is likely that eosin y is the main compound present in the extract, since the chromatogram and absorption spectrum of this extract overlaps with the *standard*.

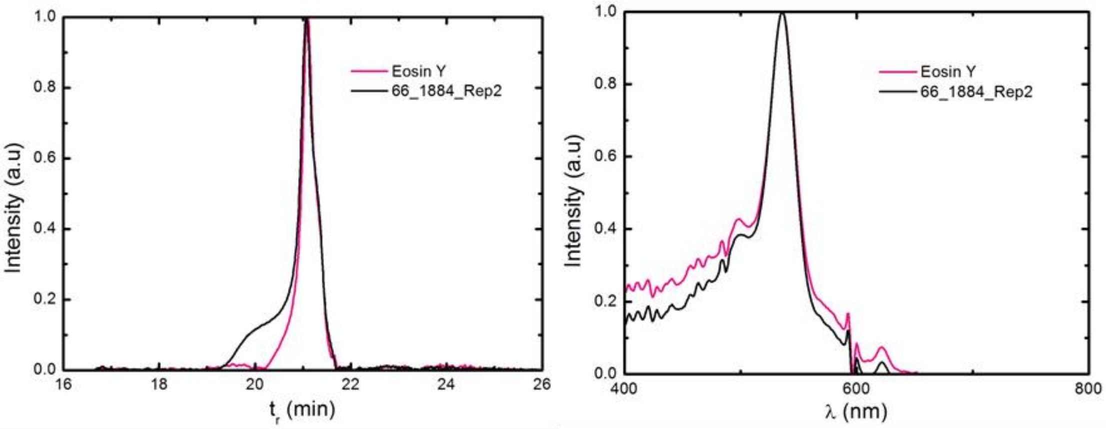

Figure 3.3.2.2- HPLC chromatograms and absorption spectra of the 66_1884_Rep2 postage stamp extract and of the standard, eosin y.

With regards to the 141_1899_Rep3 postage stamp, an identical procedure was followed; the chromatogram and absorption spectra can be seen in figure 3.3.2.3.

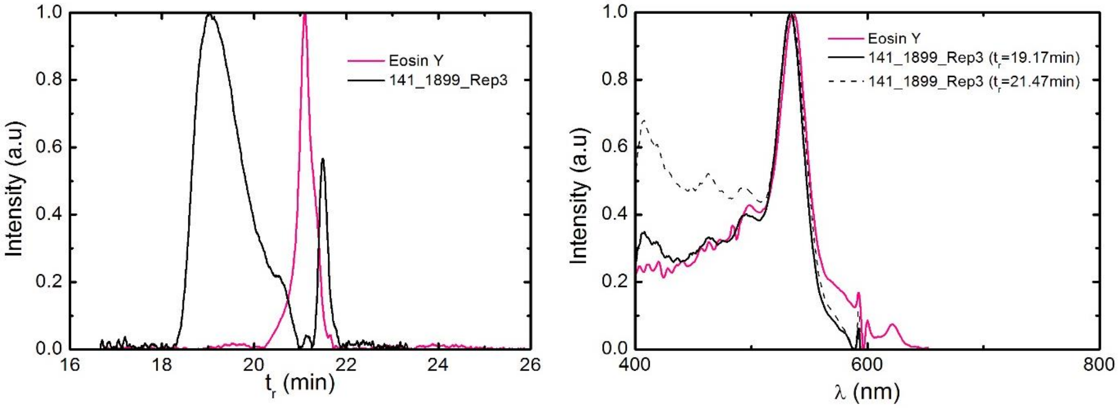

Figure 3.3.2.3- HPLC chromatograms and absorption spectra of the 141_1899_Rep3 postage stamp extract and of the standard, eosin y.

From figure 3.3.2.3, it is possible to see that this postage stamp has two peaks, separated by 2.3 minutes (see Table 3.3.2.1); however, both display the same absorption spectra which is characteristic of eosin y. These two peaks with low resolution and large width indicates that may be had occurred an overloading of the column.[12]

The retention times and the wavelengths of these postage stamps and the *standards* are summarized in Table 3.3.2.1.

Table 3.3.2.1- Retention times (obtained from HPLC-DAD) and maximum wavelength of postage stamps and the *standards,* carminic acid and eosin y.

Postage Stamp		**t_r (min)**	**λ_{max} (nm)**
			Absorption
30_1867	Rep3	7.35	493
66_1884	Rep2	21.07	499, 536
141_1899	Rep3	19.17; 21.47	496, 534
Carminic acid		7.68	483
Eosin y		21.10	498, 536

From Table 3.3.2.1, it can be seen that the retention times of the postage stamps extracts match with the *standards* and this is valid also for the absorption spectra thus showing that the postage stamps were dyed with carminic acid and eosin y.

Once identified eosin y, that is known to be strongly fluorescent, and in order to find another non-destructive technique, the fluorescence emission spectra and lifetimes in these postage stamps were additionally obtained. This will be described in the next section.

3.4 Fluorescence Emission Analysis

In this section, the results obtained for the postage stamps that was identified with eosin y as the main compound in the inked area are presented. The fluorescence emission spectra (see figure 3.4.1) of the *standard*, eosin y, was obtained in different environments: dissolved in DMSO, in solid (powder) and in paper (dye mixed in potato starch with water and painted on filter paper) form. This was then compared with the results obtained for the postage stamps, 62_1887, 66_1884, 141_1899 and 160_1909.

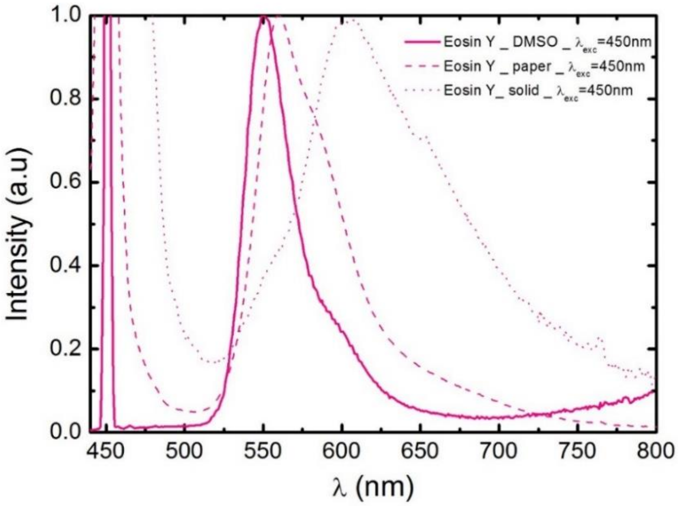

Figure 3.4.1- Emission spectra of eosin y in different environments, solution (in DMSO – solid line) and solid forms: paper (mix of dye in potato starch with water painted in filter paper – dash line), solid (powder form – dot line).

As can be seen from figure 3.4.1, depending on the chromophore environment the fluorescence spectra shows some differences[7]; *Chakraborty, M.*[11] showed that eosin y, in solution, presented two bands in the absorption spectra. They attributed to a dimeric band (at 496 nm) and the other corresponding to a monomeric band (at 517 nm). In the solution emission spectra, they verified that the band corresponding to the dimer disappeared. In this case, contrary to what was observed by *Chakraborty, M*.[11], the dimeric band is present in DMSO. In the solid state, the result was similar to which was obtained by the authors.[11]

In the next three figures (figure 3.4.2, figure 3.4.3 and figure 3.4.4), the fluorescence emission spectra of 62_1887_Rep3, 66_1884_Rep2 and 160_1909_Rep2 obtained directly from the postage stamp is presented. The remaining replicas of these postage stamps can be seen in figures A4.1 – A4.3.

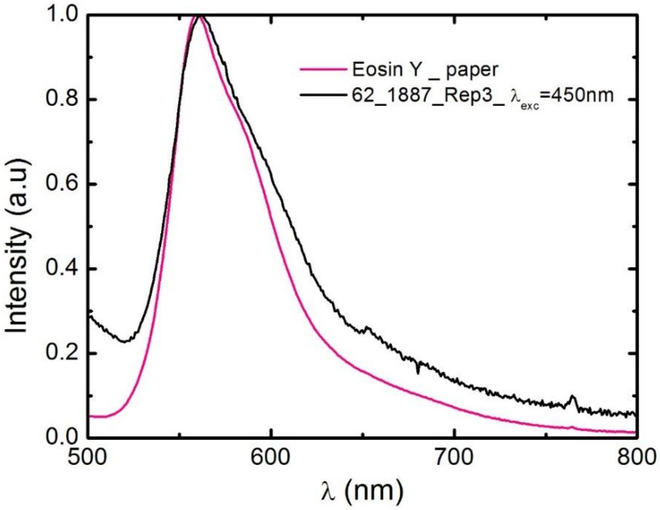

Figure 3.4.2- Emission spectra comparing the 62_1887_Rep3 postage stamp with the *standard*, eosin y (in paper form – mix of dye in potato starch with water painted in filter paper).

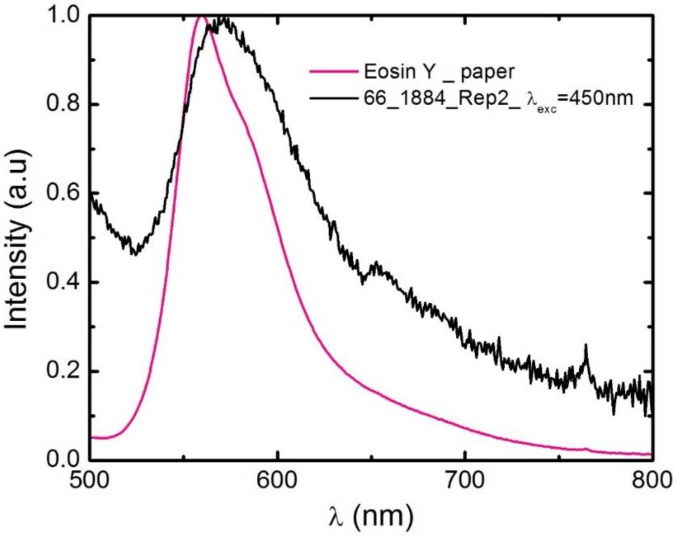

Figure 3.4.3- Emission spectra comparing the 66_1884_Rep2 postage stamp with the *standard*, eosin y (in paper form – mix of dye in potato starch with water painted in filter paper).

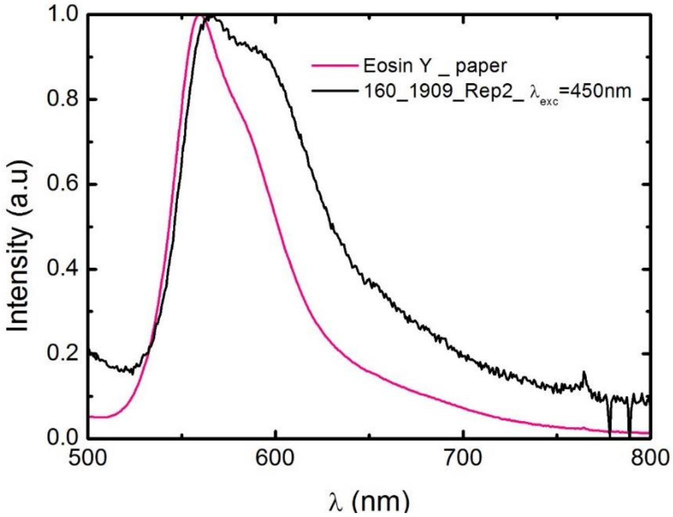

Figure 3.4.4- Emission spectra comparing the 160_1909_Rep2 postage stamp with the *standard*, eosin y (in paper form – mix of dye in potato starch with water painted in filter paper).

The next set of images (figure 3.4.5 and figure 3.4.6), show the emission spectra of the dye extracted from the postage stamps, 141_1899_Rep3 and 160_1909_Rep3, respectively, dissolved in DMSO.

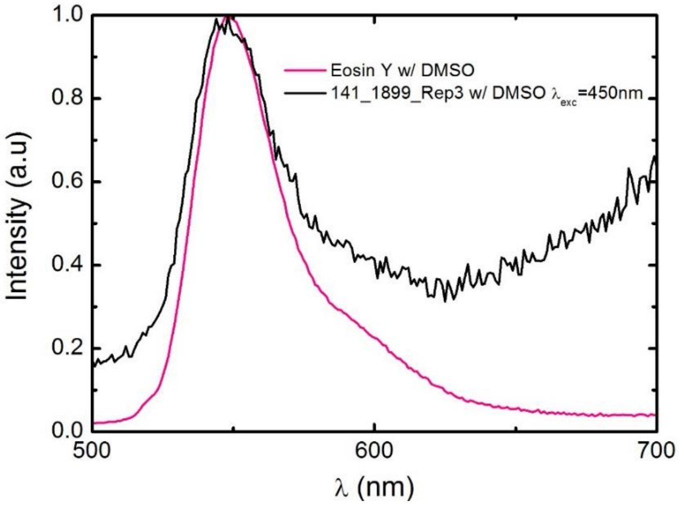

Figure 3.4.5- Emission spectra comparing the 141_1899_Rep3 postage stamp with the *standard*, eosin y, in DMSO.

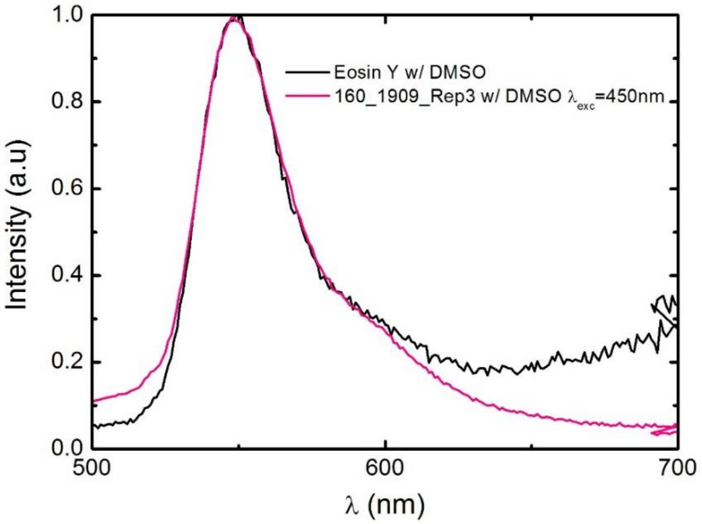

Figure 3.4.6- Emission spectra comparing the 160_1909_Rep3 postage stamp with the *standard*, eosin y, in DMSO.

All the spectra were obtained with λ_{exc}=450 nm. As can be seen from the figures 3.4.2, 3.4.3 and 3.4.4, a perfect match between the postage stamp and the *standard* (figure 3.4.2) is observed; in the remaining figures the match is nearly perfect. The difference between the wavelength maxima of the postage stamps and the *standard,* showed in Table 3.4.1, is small. This difference can be due to the heterogeneity of the samples and the difficulty of having a good inked area to obtain the fluorescence emission spectra.

Although, they corroborate the presence of eosin y in these samples confirming what had already observed with the other techniques (non-destructive and destructive). In the remaining replicas of these postage stamps the results were similar, as can be seen in figures A4.1 – A4.3, confirming once more the presence of eosin y.

For the solutions, the results were even better, as illustrated in figures 3.4.5 and 3.4.6. If the 141_1899_Rep3 has a good overlap with the *standard*, the 160_1909_Rep3 sample has an even better match with a lower difference between the wavelength maxima of the postage stamps and the eosin y (spectral data showed in Table 3.4.1).

It was also possible to see the difference in the postage stamps and the eosin y either in “solid state” or in the “solution state”. For *standard,* the wavelength maxima in solution was 549 nm and in “solid state” (the mixture of the dye with potato starch and water, painted on filter paper) was 560 nm. The conditions that were made to obtain the best form to compare with the postage stamps show that the mimic of the solid state of postage stamps had a good achievement, proving that the identification of the postage stamp without damage is possible.

In Table 3.4.1 fluorescence quantum yields of the postage stamps is summarised. For the 62_1887 postage stamps, the three replicas, the ϕ_f values are in the range 0.012 - 0.02, while for the two replicas of the 66_1884 postage stamps the values are between 0.003 and 0.006 and finally for the 160_1909 postage stamps (three replicas) the values range is 0.005 - 0.012. Only for the eosin y (in paper) the quantum yield value obtained was similar to the other study[12], 0.20 in water, may be because the mixture was also prepared with water. The differences in the quantum yield values are likely to mirror a fade of eosin y (with consequent formation of less emissive photo degradation products).

Table 3.4.1- Emission maxima of eosin y [in the solid (powder form), paper (dyes mixed with potato starch and painted in filter paper) and in solution (DMSO)] and postage stamps (and replicas) [investigated in the solid (direct analysis of the postage stamps) and in solution (extracted from the postage stamps)] and quantum yields.

Postage Stamp			**λ_{max} (nm)**	**Φ_f**
			Emission	
62_1887	Rep1		572	0.017
	Rep2		572	0.012
	Rep3		562	0.020
66_1884	Rep1		572	0.003
	Rep2		569	0.006
141_1899	Rep1		–	–
	Rep2		–	
	Rep3	Paper	–	–
		Solution (DMSO)	548	
160_1909	Rep1		557	0.005
	Rep2		565	0.009
	Rep3	Paper	565	0.012
		Solution (DMSO)	550	
Eosin y	Solution (DMSO)		549	ND
	Paper		560	0.216
	Solid		604	0.016

3.5 Time-Resolved Fluorescence Analysis

To complement the analysis made in the previous section, the fluorescence decays of the postage stamps discussed before were measured. The experimental conditions were made using the postage stamp intact and then compared with the *standard* in the mimetic condition (mixture of the dye with potato starch and water painted on filter paper, see figure 3.5.1) and in solution (see figure 3.5.2).

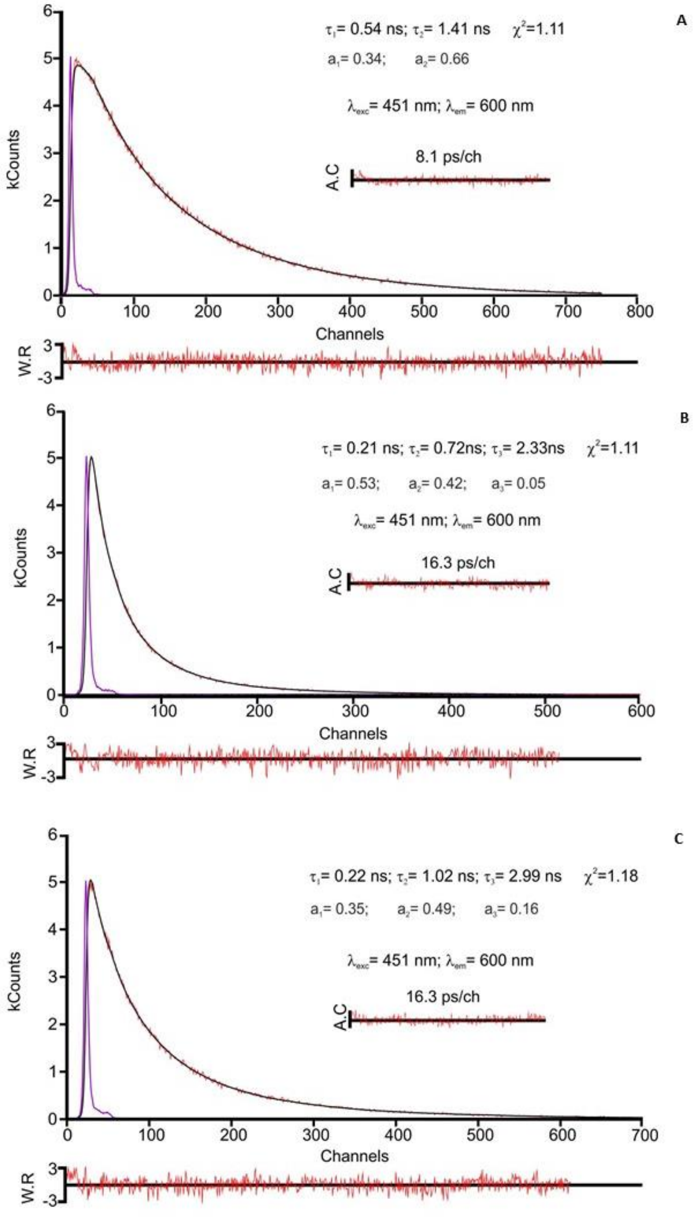

Figure 3.5.1- Fluorescence decays of (**A**) eosin y, in asheless filter paper, (**B**) 62_1887_Rep1 and (**C**) 160_1909_Rep3 postage stamps.

From the figure 3.5.1, it can be seen that the fluorescence decays are multiexponential, reflecting the different environments proved by eosin y in the mimetic form. Analysis of the decays shows that these are best-fitted with a tri-exponential decay law. The lifetime values of the postage stamps are close to those obtained for eosin y in the mimetic environment. For the others replicas, the same multiexponential result was obtained, as can be seen in Table 3.5.1.

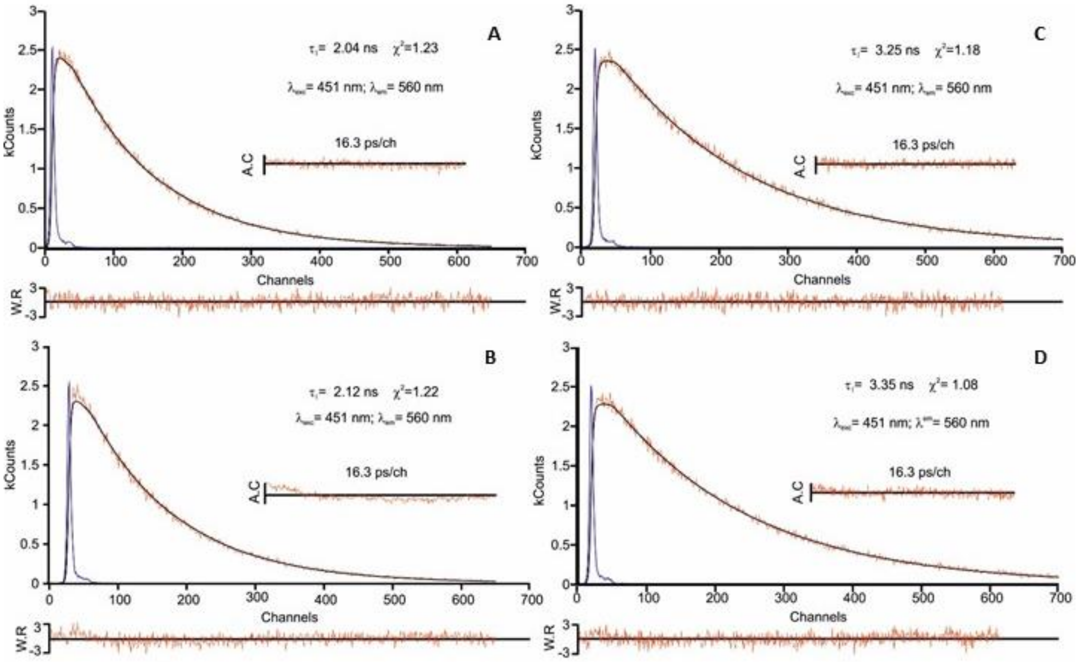

Figure 3.5.2- Fluorescence decays of (**A**) eosin y in MeOH:H_2O, (**B**) 66_1884_Re2 postage stamp extract in MeOH:H_2O, (**C**) eosin y in DMSO and (**D**) 141_1899_Rep3 postage stamp extract in DMSO.

From the figure 3.5.2, it can be seen that, in both the solvent (MeOH:H_2O and DMSO), the *standard* and the extract (obtained from the postage stamp) display identical lifetime values, thus showing that eosin y is present in these postage stamps. The values obtained for the eosin y in methanol:water were found close to what is reported *in Robinson, G.W.*[13], and in fact, it is single exponential as reported by *Chakraborty, M.*[11], further validating the presence of this dye in the analysed postage stamps.

The fluorescence decays of the postage stamps (Table 3.5.1) are fitted with tri-exponential decays, as already mentioned, mirroring the heterogeneity of the solid media.

However, in the case of the 160_1909 postage stamps, the major components, as given by the fractional contribution (C_i) of each species, is associated with the two longer components (with more than 90% of the contribution); the longer components although displaying a value that is ca. one half of the solution lifetime can be clearly related to an excited species associated to the “isolated” eosin y. In the case of the postage stamps 62_1887 and 66_1884, it is the intermediate component that dominates the decay with more than 50% of the contribution.

Table 3.5.1- Time resolved fluorescence data obtained for the different postage stamps. Decay times: τ_i, pre-exponential factors (A_i) and $\%C_i$ the fractional contribution (Ci) of each species at the λ_{em}.

Stamp		Scale(ps/ch)	λ_{exc} (nm)	λ_{em} (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	A_1	A_2	A_3	$\%C_1$	$\%C_2$	$\%C_3$
62_1887_Re1		16.3	451	600	0.21	0.72	2.33	0.53	0.42	0.05	21.11	56.48	22.41
62_1887_Rep2					0.17	0.70	2.38	0.57	0.37	0.06	19.95	52.80	27.25
62_1887_Rep3					0.23	1.04	3.86	0.46	0.47	0.07	12.33	56.00	31.67
66_1884_Rep1		8.1			0.12	0.43	1.37	0.52	0.39	0.09	17.56	46.52	35.92
66_1884_Rep2	**Paper**				0.07	0.31	1.30	0.53	0.41	0.06	15.16	52.72	32.12
	Solution w/ MeOH:H_2O	16.3		560	2.12	–		1–	–		100 –	–	
141_1899_Rep3 (solution w/ DMSO)		16.3		560	3.35	–		1–	–		100 –	–	
160_1909_Rep1		16.3		600	0.18	0.94	3.31	0.47	0.42	0.11	9.94	46.39	43.67
160_1909_Rep2					0.13	0.55	2.00	0.47	0.38	0.15	10.60	36.23	53.18
160_1909_Rep3	**Paper**				0.22	1.02	2.99	0.35	0.49	0.16	7.43	47.49	45.08
	Solution w/ DMSO			560	2.81	6.05		0.80	0.20		64.34	35.66_	
Eosin y	**Paper**	8.1	451	600	0.54	1.41		0.34	0.66		16.60	83.40_	
	Solution w/ H_2O:MeOH	16.3			2.01	_		1_	_		100 _	_	
	Solution w/ DMSO			560	3.25	_		1_	_		100 _	_	
	Solution w/ DMSO				3.37	_		1_	_		100 _	_	

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Chapter IV

Conclusions

Analysis of the dyes and pigments (the molecules of colour) used to dye the first Portuguese postage stamps has been done for the first time. Both destructive and non-destructive analysis of the postage stamps was performed.

The main question made at the beginning of this work – What were the dyes/pigments used in the first Portuguese postage stamps? – was answered. In particular both organic and inorganic molecules of colour were identified in the different postage stamps analyzed.

From XRF analysis, cinnabar, lead oxides, lead sulfide and lead chromate were identified.

From UV-Vis, HPLC-MS and HPLC-DAD analysis carminic acid and eosin y were identified as the organic dyes present in several of the analyzed specimens.

Steady state and time resolved fluorescence techniques were used for the first time in the identification of the eosin y in postage stamps, leading to the development of a non-destructive procedure for the identification of these colouring materials.

Appendix

Appendix

Appendix I – XRF Analysis

The results here presented are in cps (counts per second), i.e., number of photons were detected. When only 1 or 2 specimens in each year, like in 25_1867 (2 replicas), 66_1884 (2 replicas), 69_1892-94 (1 replica) and 150_1898 (2 replicas), were done more analyzes in same postage stamp but in other area in order to make a total of 3 replicas. In Table A1, the data are organized by catalogue number and printing year of postage stamps, e.g, 150_1898, and in each year have the replicas that were analyzed. In the replicas columns there are two different results, the first one – D+P (dye + paper) – has the contribution of elements present in ink and in the paper; the second column – D – (only dye) shows the elements that are present only in the dye (after the subtraction of paper information). Some results have a highlight because their unexpected presence, either by the elements itself either by the counts that this element may have.

Table A1 – Summarized data of all Portuguese postage stamps by XRF.

	13_1857-62						16_1862-66						22_1866					
	Rep.1		*Rep.2*		*Rep.3*		*Rep.1*		*Rep.2*		*Rep.3*		*Rep.1*		*Rep.2*		*Rep.3*	
	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D
Al	46,0	1,5	48,4	-	-	-	-	-	44,8	-	-	-	-	-	41,1	-	43,1	-
P	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
S	-	-	-	-	-	-	-	-	-	-	-	-	559,4	320,8	95,1	-	180,5	26,8
Cl	132,7	-	137,5	-	146,8	-	-	-	127,7	4,8	141,6	4,8	185,3	7,8	146,3	4,8	219,1	-
K	535,6	6,5	590,1	-	532,8	27,6	376,3	-	510,1	-	405,5	33,6	463,2	39,0	391,2	32,8	458,1	22,5
Ca	619,8	78,3	711	139,92	594,7	152,6	1105,1	210,4	973,9	183,6	1406,1	336,4	4193,1	871,8	712,2	107,0	2058,4	385,7
Ti	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cr	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mn	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fe	1773,1	5,7	1838,2	7,38	1796,5	41	19,9	-	1718,4	17,0	1592,2	50,6	20,5	-	1590,3	41,8	1652,9	76,8
Cu	-	-	17,5	1,13	16,8	-	16,2	-	17,3	0,4	16,3	-	17,2	-	16,4	-	19,6	1,3
Zn	-	-	17,8	-	17,1	0,6	15,9	-	-	-	17,3	-	22,8	2,6	24,1	4,5	17,9	1,0
As	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Br	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sr	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sn	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ba	-	-	-	-	-	-	-	-	-	-	-	-	735,0	-	-	-	-	-
Hg	-	-	-	-	-	-	-	-	-	-	-	-	88,1	71,9	13,7	-	14,7	0,8
Pb	29,7	-	24,6	-	19,3	1,5	19,2	1,9	22,6	3,1	21,2	3,2	20,4	1,4	20,0	2,0	20,8	2,7

	25_1867						30_1867						40_1870-79					
	Rep.1		*Rep.2*		*Rep.3*		*Rep.1*		*Rep.2*		*Rep.3*		*Rep.1*		*Rep.2*		*Rep.3*	
	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D
Al	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
P	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
S	622,8	335,2	330,6	232,9	-	-	599,4	200,0	444,3	154,2	617,1	70,2	136,2	-	526,7	150,2	689,2	-
Cl	247,2	70,7	231,8	43,2	245,1	55,0	-	-	-	-	-	-	266,1	8,1	182,0	2,6	196,7	-
K	-	-	498,4	113,5	471,7	83,0	-	-	401,6	32,5	453,0	-	-	-	507,5	114,2	595,4	122,7
Ca	2567,6	-	1043,1	21,8	1160,9	131,5	4621,1	175,3	5782,3	-	6227,2	255,7	730,6	198,0	5608,0	673,6	8156,7	1172,9
Ti	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cr	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mn	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fe	1633,7	104,4	1637,5	37,5	1704,9	112,8	1496,6	14,0	1430,4	42,7	1528,6	56,2	1585,1	133,0	1425,6	-	1424,8	-
Cu	18,1	0,4	17,2	0,5	17,5	-	17,5	0,5	17,6	0,6	20,00	2,0	18,3	2,7	17,5	1,2	17,4	0,6
Zn	21,2	-	18,4	0,2	18,8	0	21,7	4,0	16,5	-	18,1	1,8	18,7	-	18,3	-	19,1	2,0
As	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Br	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	36,0	5,4
Sr	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sn	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ba	1069,2	521,5	1145,0	573,8	1171,3	597,1	783,7	274,4	-	-	-	-	668,7	-	-	-	-	-
Hg	-	-	-	-	-	-	76,8	62,4	-	-	37,1	21,2	-	-	-	-	-	-
Pb	256,3	235,6	179,8	147,2	172,1	138,2			18,9	1,0	-	-	23,7	1,6	34,6	16,6	28,6	10,2

	54_1880						62_1887						63_1887-90_LR					
	Rep.1		*Rep.2*		*Rep.3*		*Rep.1*		*Rep.2*		*Rep.3*		*Rep.1*		*Rep.2*		*Rep.3*	
	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D
Al	45,3	3,5	-	-	-	-	-	-	95,8	20,0	96,0	16,1	-	-	-	-	-	-
P	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
S	-	-	636,3	484,2	-	-	1705,8	1377,7	1663,8	1411,4	1599,3	1188,2	1589,4	1401,7	1653,4	1459,6	1836,5	1669,8
Cl	277,7	135,1	296,2	126,9	402,4	228,8	-	-	-	-	349,1	-	-	-	-	-	-	-
K	-	-	468,5	53,7	490,6	73,2	549,3	-	517819,0	-	508,0	-	-	-	-	-	-	-
Ca	687,4	37,6	591,0	55,7	665,9	78,2	714,9	-	914,4	-	522,1	-	847,4	-	911,2	-	856,0	-
Ti	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cr	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mn	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fe	1624,9	18,8	1625,1	38,7	1668,6	54,9	524,7	-	386,7	-	420,8	-	333,7	-	356,3	-	342,7	-
Cu	18,6	2,0	17,0	0,7	17,3	1,0	14,9	-	14,9	-	14,5	-	14,4	0,0	14,6	-	15,7	-
Zn	42,2	21,8	31,4	15,2	24,3	7,4	-	-	14,8	-	14,2	-	18,8	-	17,1	-	20,6	-
As	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Br	-	-	-	-	-	-	-	-	59,5	38,0	44,4	18,1	-	-	-	-	-	-
Sr	-	-	-	-	-	-	662,1	13,7	658,4	-	840,9	0,4	746,7	-	664,7	28,6	767,1	49,6
Sn	464,2	118,8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ba	-	-	576,6	-	-	-	23739,3	10721,2	24844,5	8408,3	24124,3	4792,6	25182,9	9479,6	24953,6	10105,7	27490,8	12751,0
Hg	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pb	814,3	718,5	702,5	545,8	1111,9	1026,3	76,2	52,9	218,2	196,0	108,9	18,1	17,3	-	19,5	-	18,3	-

Table A1 – Summarized data of all Portuguese postage stamps by XRF (continuation).

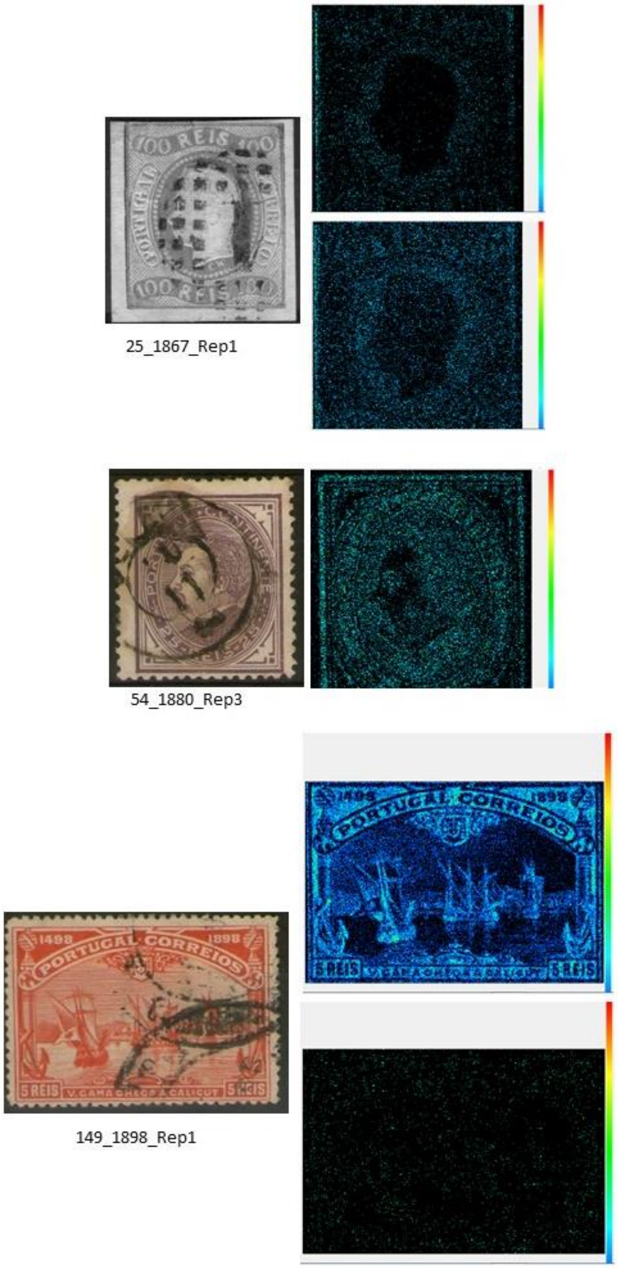
	63_1887-90_VA						66_1884						69_1892-94					
	Rep.1		*Rep.2*		*Rep.3*		*Rep.1*		*Rep.2*		*Rep.3*		*Rep.1*		*Rep.2*		*Rep.3*	
	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D
Al	-	-	-	-	98,0	23,7	96,9	29,8	96,8	31,8	101,3	37,1	105,0	61,7	104,0	58,1	107,1	65,3
P	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
S	1717,4	1510,1	1680,3	1515,3	1764,3	1488,5	1717,4	1548,8	1681,4	1521,3	1764,9	1584,8	310,9	217,0	322,6	226,0	322,0	19,0
Cl	420,9	79,6	-	-	-	-	-	-	-	-	-	-	279,2	22,1	281,5	-	292,7	9,4
K	529,5	-	535,3	-	536,7	-	464,8	-	478,8	-	505,1	-	899,6	269,7	864,2	155,7	915,3	229,9
Ca	991,2	-	910,1	29,6	904,7	-	638,9	-	680,6	-	713,7	-	2068,1	373,2	2208,2	562,3	2153,9	284,4
Ti	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cr	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mn	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fe	618,8	-	618,0	-	455,0	-	408,0	-	365,2	-	368,1	-	2040,2	46,9	1964,3	5,8	2053,0	90,5
Cu	15,6	-	15,3	-	14,0	-	15,4	-	-	-	16,4	0,2	-	-	17,5	1,4	18,4	1,7
Zn	18,6	-	15,0	-	14,3	-	14,8	-	-	-	14972,0	-	-	-	16,6	1,4	-	-
As	-	-	-	-	-	-	-	-	-	-	-	-	83,3	63,3	88,6	65,1	77,8	58,5
Br	46,8	22,4	42,3	20,9	30,2	9,0	76,2	46,5	74,7	46,1	-	-	-	-	-	-	-	-
Sr	780,8	0,4	952,0	77,4	844,4	20,6	875,5	-	1080,5	44,2	1136,5	85,7	-	-	-	-	-	-
Sn	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ba	24368,7	9569,3	26147,8	12028,7	27227,6	11319,4	25145,5	10268,8	26038,5	12193,7	27136,4	11461,2	1447,2	415,6	1499,8	367,7	1529,1	471,0
Hg	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pb	39,0	13,5	44,3	19,9	28,2	7,3	73,8	43,0	75,6	47,3	73,9	47,4	-	-	88,6	65,1	-	-

Table A1 – Summarized data of all Portuguese postage stamps by XRF (continuation)

	130_1895						**141_1899**						**149_1898**					
	Rep.1		*Rep.2*		*Rep.3*		*Rep.1*		*Rep.2*		*Rep.3*		*Rep.1*		*Rep.2*		*Rep.3*	
	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D
Al	48,7	6,8	45,1	4,5	63,6	13,0	61,1	6,3	50,6	-	62,9	12,8	67,4	14,8	65,3	11,9	65,8	14,3
P	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
S	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cl	161,7	15,6	149,9	-	183,4	-	168,7	-	190,6	2,6	236,1	3,2	781,0	577,0	765,3	434,2	790,9	431,8
K	382,8	32,5	388,5	12,8	792,6	107,2	608,6	0,6	568,5	-	577,0	19,7	355,6	-	393,9	-	403,7	-
Ca	532,3	14,2	524,9	-	610,6	23,2	625,9	41,0	814,6	-	589,7	88,5	1027,6	518,9	904,2	416,3	866,1	354,4
Ti	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cr	-	-	-	-	-	-	-	-	-	-	-	-	1606,0	588,9	1559,4	576,1	1516,1	535,2
Mn	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fe	1666,9	10,8	1587,0	-	1816,3	5,3	1693,1	-	1600,9	22,3	1698,4	37,1	1252,7	-	1463,4	-	1470,3	-
Cu	17,1	-	15,8	-	14,4	0,1	-	-	16,4	0,4	19,1	4,1	-	-	20,7	5,1	-	-
Zn	18,6	1,4	16,0	0,0	14,7	-	-	-	20,5	0,8	20,1	5,0	-	-	25,8	7,8	27,7	8,2
As	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Br	-	-	-	-	-	-	94,4	63,7	-	-	143,9	113,3	-	-	-	-	-	-
Sr	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sn	118,1	4,4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ba	829,4	240,6	838,7	253,9	622,1	37,6	-	-	829,9	5,2	-	-	532,6	-	534,9	-	549,7	-
Hg	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pb	20,1	0,2	17,9	-	17,5	0,4	48,5	27,6	30,9	9,4	61,8	42,5	5702,6	5468,5	3503,7	3410,3	3954,6	3815,2

	150_1898						156_1909						160_1909					
	Rep.1		*Rep.2*		*Rep.3*		*Rep.1*		*Rep.2*		*Rep.3*		*Rep.1*		*Rep.2*		*Rep.3*	
	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D	D+P	D
Al	72,8	20,7	-	-	-	-	81,1	-	91,2	-	95,9	-	88,8	-	91,5	-	86,4	4,7
P	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
S	-	-	-	-	-	-	448,4	-	441,7	322,3	-	-	-	-	406,1	-	503,9	92,1
Cl	763,5	393,9	757,0	521,8	707,3	454,1	174,4	-	162,8	10,3	255,6	30,7	165,5	13,7	262,0	-	258,1	46,6
K	440,7	-	455,0	-	490,9	-	730,2	-	826,2	-	960,4	30,9	825,2	-	873,1	-	737,9	-
Ca	3224,1	2799,3	3870,7	3167,9	3271,5	2574,3	2610,8	990,4	2947,6	1873,5	3109,7	1289,9	972,2	189,7	4049,2	-	3549,3	2367,9
Ti	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cr	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mn	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fe	1425,9	-	1134,3	-	1331,0	-	1616,8	-	1935,3	-	1889,8	-	1969,1	-	1821,1	161,2	1715,6	-
Cu	22,0	5,2	23,0	6,8	22,3	5,5	16,8	-	18,0	0,7	17,6	-	18,0	-	19,3	0,8	17,7	0,7
Zn	28,9	11,9	32,1	10,6	27,5	3,5	16,2	-	21,3	-	29,2	0,4	22,7	0,9	20,1	1,4	28,0	6,3
As	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Br	-	-	-	-	-	-	-	-	-	-	-	-	42,3	12,0	71,4	41,6	78,6	45,2
Sr	-	-	-	-	-	-	284,8	-	-	-	-	-	-	-	-	-	288,2	-
Sn	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ba	1463,2	935,2	1523,7	1016,6	1323,0	833,8	4625,5	-	709,6	168,4	665,0	155,9	-	-	-	-	4248,4	128,2
Hg	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pb	4069,1	3987,3	5402,7	5227,8	4152,5	3862,3	25,8	0,3	46,9	5,2	21,9	-	50,0	29,7	54,3	34,3	61,4	38,0

In Figure A1.1, some of the others mappings obtained for postage stamps are present, for 25_1867_Rep1 mapping of Pb (above) and S (below), for 54_1880_Rep3 mapping of Pb and for 141_1898_Rep1 of Pb (above) and Cr (below). The results of others replicas (25_1867_Rep2, 54_1880_Rep1 and 54_1880_Rep3) are not shown in the figure because the same result was obtained.



25_1867_Rep1

54_1880_Rep3

149_1898_Rep1

Figure A1.1 – Mappings of 25_1867_Rep1, 54_1880_Rep3 and 149_1898_Rep1 postage stamps for Pb and Cr. Acquisition conditions: current at 1000 µA; collimator at 0.2x0.2mm; time per pixel 50,00 ms; in 25_1867_Rep1, 54_1880_Rep3 pixel size 60 µm/pixel, for Pb voltage at 50kV with filter for Pb; in 25_1867_Rep1 for S voltage at 15kV without filter; in 149_1898_Rep1 pixel size 70 µm/pixel, for Pb voltage at 50kV with filter for Pb and for Cr voltage at 15kV with filter for Cr.

In Figure A1.2, is depicted the mapping of 69_1892-94 postage stamp for the As.

Figure A1.2 – Mapping of 69_1892-94 postage stamp for As. Acquisition conditions: current at 1000 µA; collimator at 0.2x0.2mm; pixel size 70 µm/pixel; time per pixel 50,00 ms; voltage at 50kV; filter: for Pb.

Appendix II – UV-Vis Analysis

The absorption spectra of the postage stamps and the standards are present in several images (Figure A2.1, Figure A2.2, Figure A2.3, Figure A2.4 and Figure A2.5) corresponding to the samples 13_1857-62_Rep2/Rep3, 22_1866_Rep2/Rep3 and 30_1887_Rep2, 62_1887_Rep2/Rep3, 63_1887-90_LR_Rep1 and 160_1909, respectively.

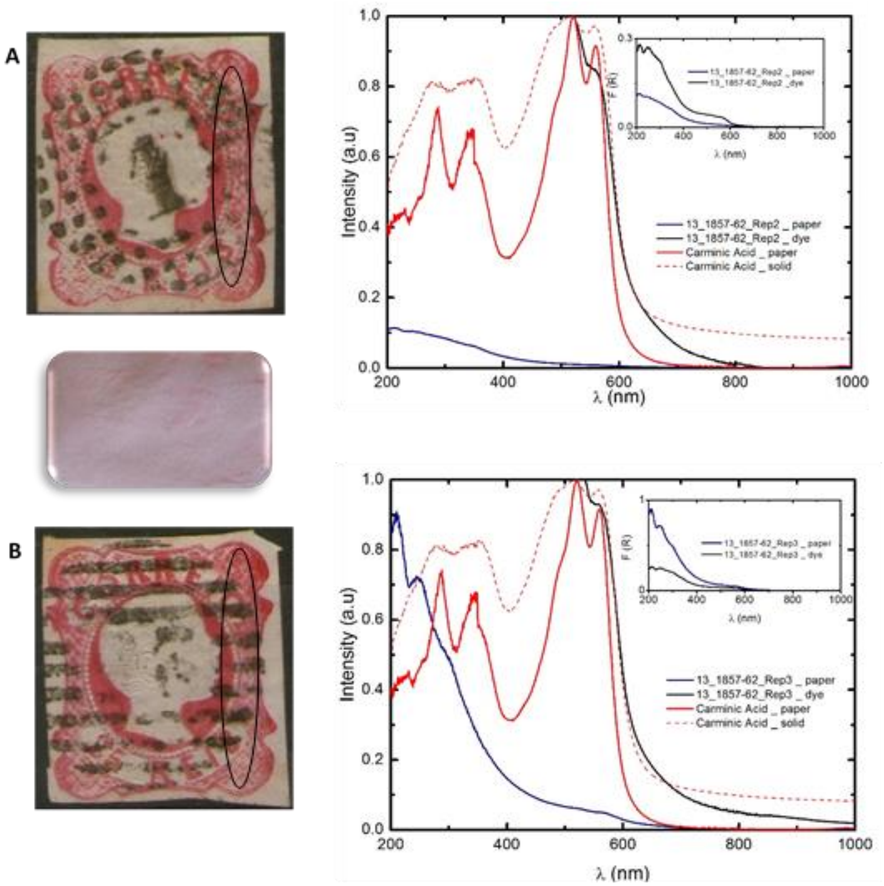


Figure A2.1- Absorption spectra comparing the (**A**) 13_1857-62_Rep2 and (**B**) 13_1857-62_Rep3 postage stamps – *paper*: back of the stamp; *dye*: coloured area (shown in the image by a circle) – with a *standard*, carminic acid – *paper*: filter paper painted with the standard; *solid*: standard in the powder form.

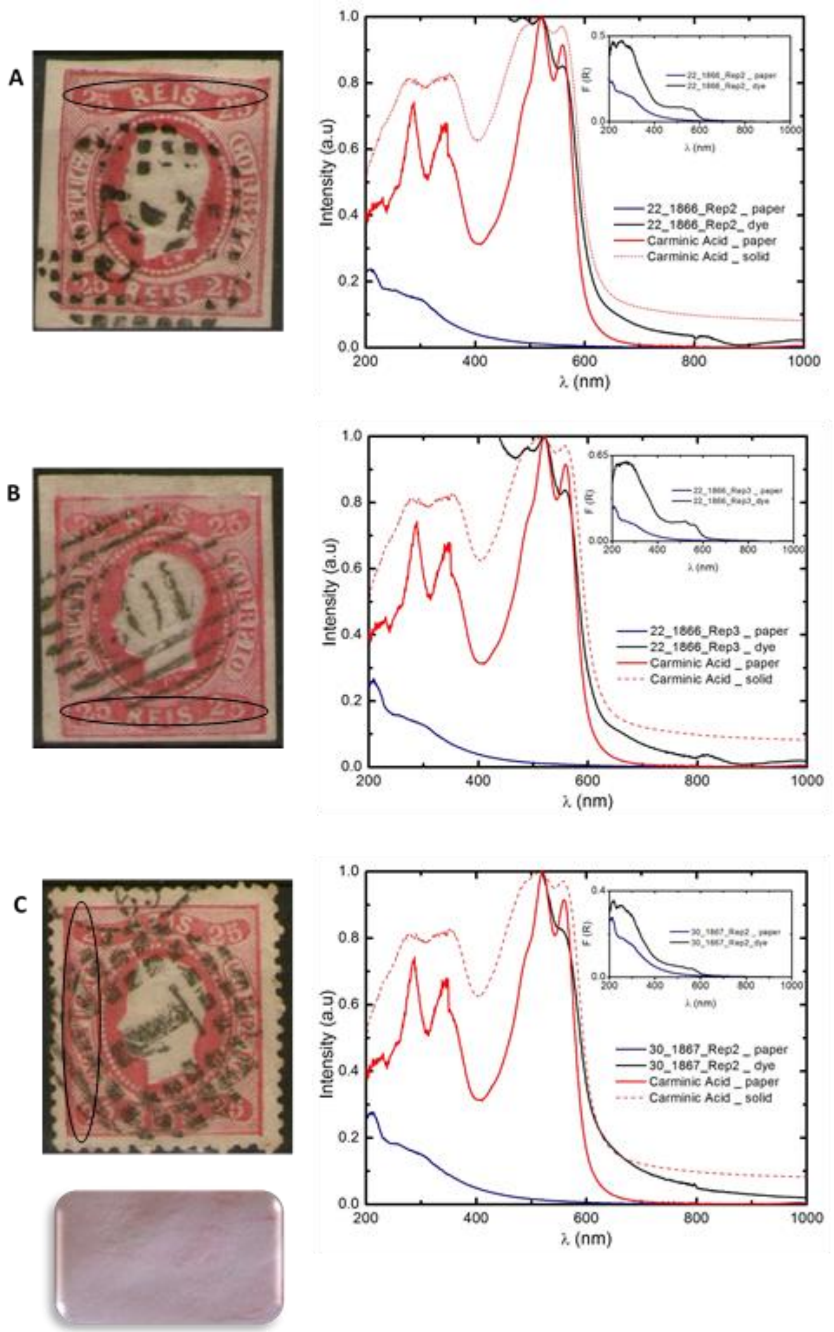


Figure A2.2- Absorption spectra comparing the (**A**) 22_1866_Rep2, (**B**) 22_1866_Rep3 and (**C**) 30_1867_Rep2 postage stamps – *paper*: back of the stamp; *dye*: coloured area (shown in the image by a circle) – with a *standard*, carminic acid – *paper*: filter paper painted with the standard; *solid*: standard in the powder form.

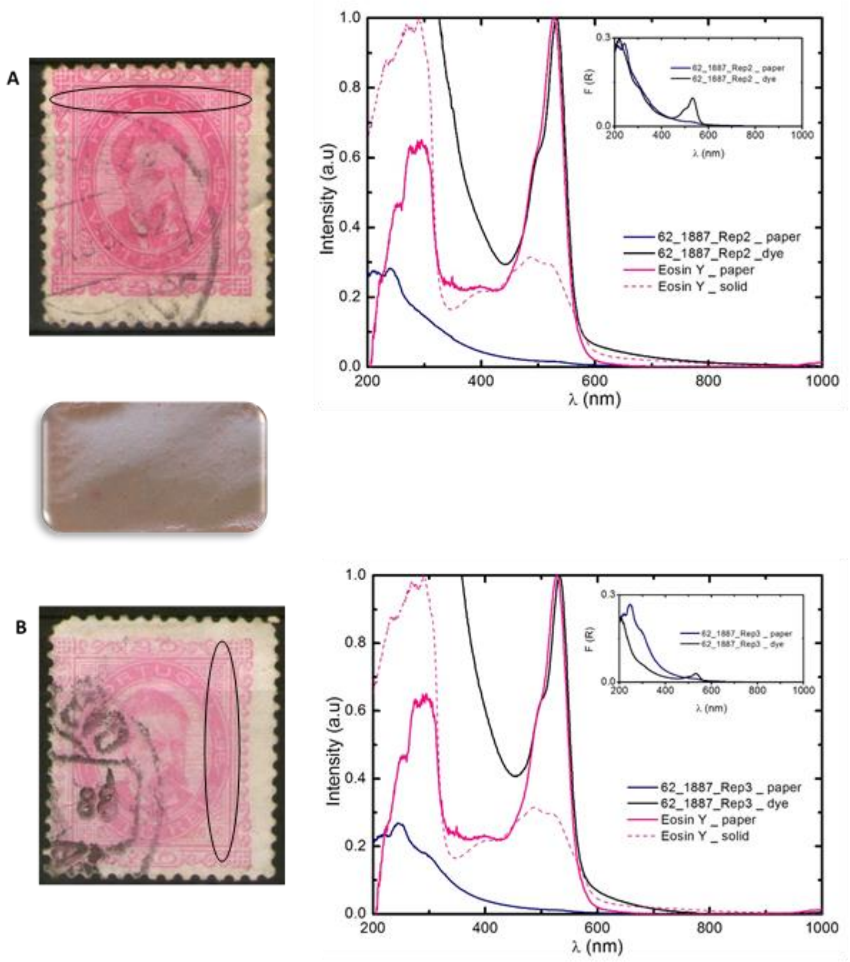


Figure A2.3- Absorption spectra comparing the (**A**) 62_1887_Rep2, (**B**) 62_1887_Rep3 postage stamps – *paper*: back of the stamp; *dye*: coloured area (shown in the image by a circle) – with a *standard*, eosin y– *paper*: filter paper painted with the standard; *solid*: standard in the powder form.

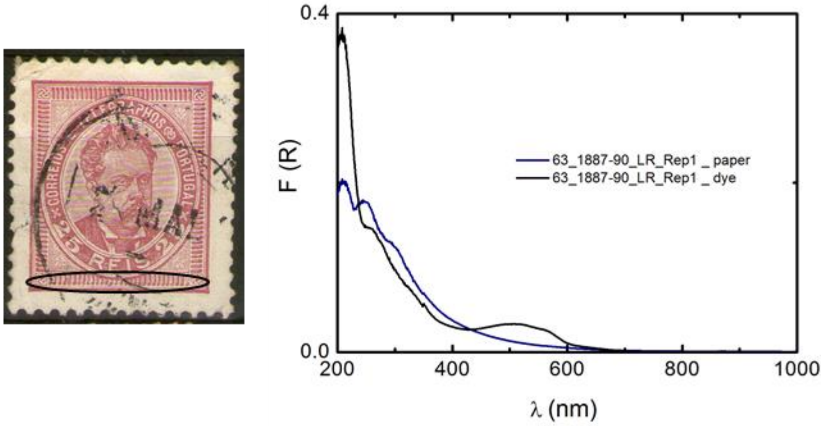


Figure A2.4- Absorption spectrum of 63_1887-90_LR_Rep1 postage stamp – *paper*: back of the stamp; *dye*: coloured area (shown in the image by a circle).

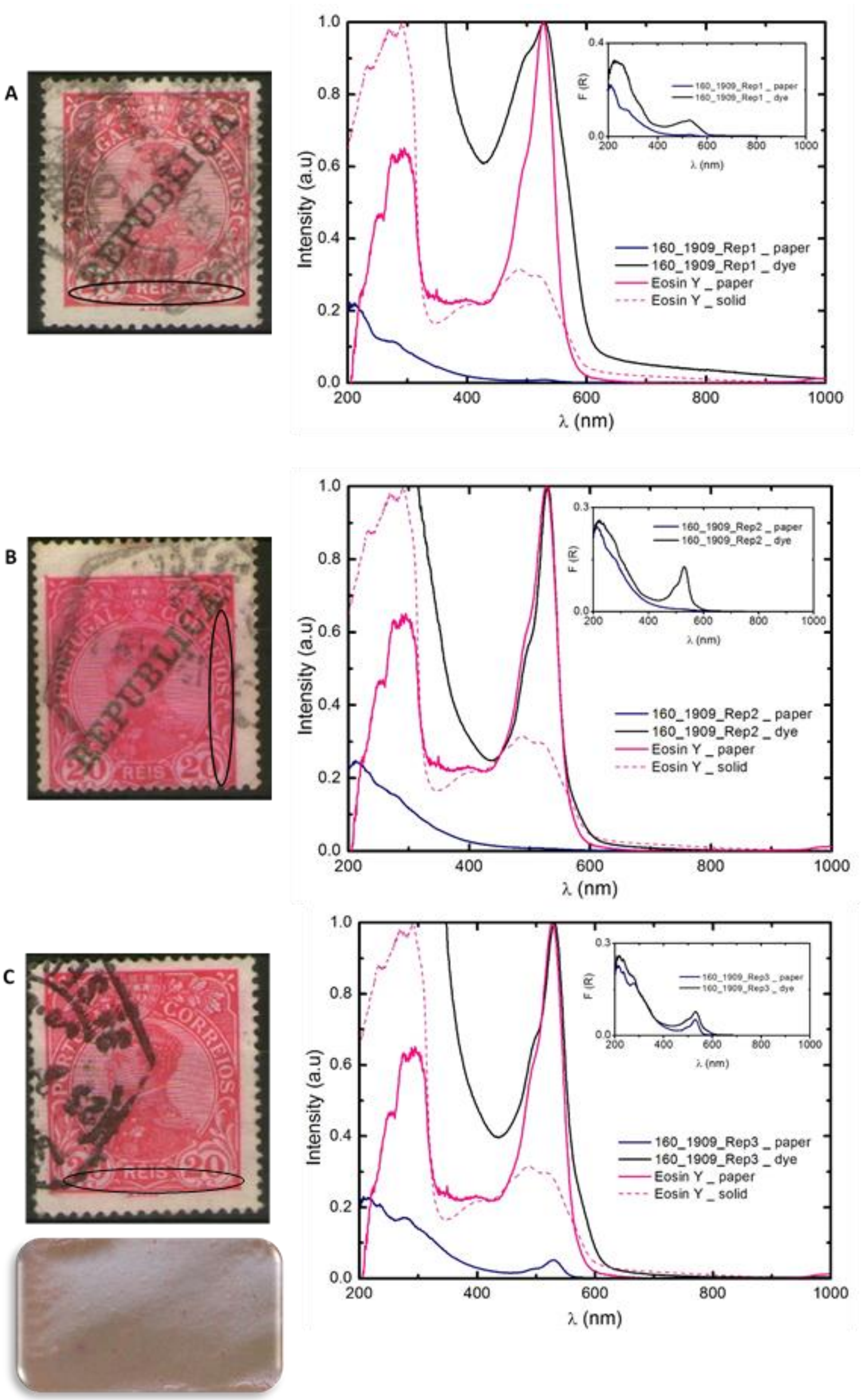


Figure A2.5- Absorption spectra comparing the (**A**) 160_1909_Rep1, (**B**) 160_1909_Rep2 and (**C**) 160_1909_Rep3 postage stamps – *paper*: back of the stamp; *dye*: coloured area (shown in the image by a circle) – with a *standard*, eosin y– *paper*: filter paper painted with the standard; *solid*: standard in the powder form.

Appendix III – HPLC-MS Analysis

In the following section, the results obtained for the remaining replicas of the postage stamps that were analyzed by HPLC-MS are shown. The 13_1857-62_Rep2 and Rep3, 16_1862-66_Rep2 and Rep3, 22_1866_Rep3 & 30_1867_Rep2 and 40_1870-79_Rep2 and Rep3 postage stamps are present in Figure A3.1, Figure A3.2, Figure 3.3 and Figure 3.4, respectively.

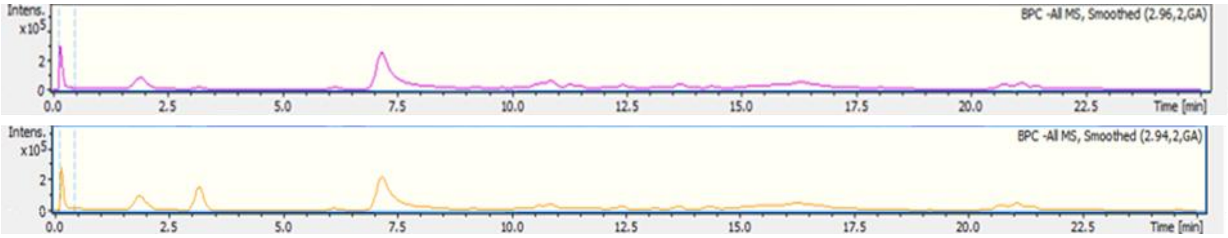


Figure A3.1– Total ion chromatograms obtained by LC-HRMS/ESI (-) for the 13_1857-62_Rep2 (*purple*) and 13_1857-62_Rep3 (*orange*) postage stamps.

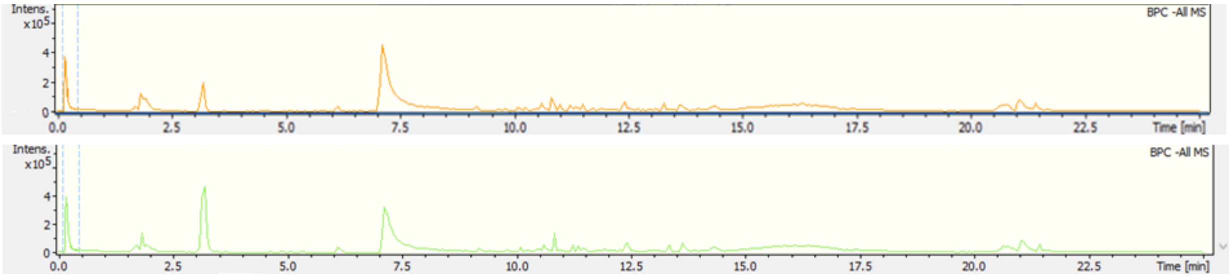


Figure A3.2– Total ion chromatograms obtained by LC-HRMS/ESI (-) for the 16_1862-66_Rep2 (*orange*) and 16_1862-66_Rep3 (*green*) postage stamps.

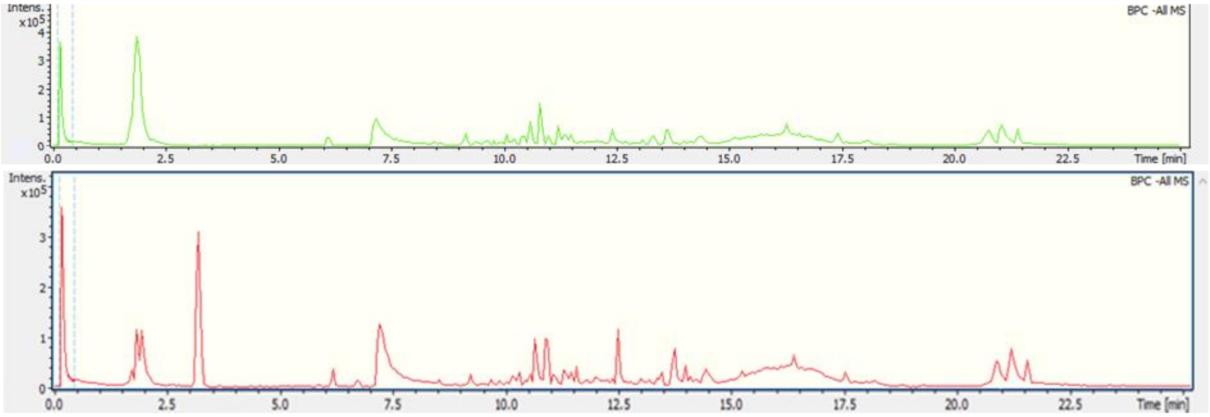


Figure A3.3– Total ion chromatograms obtained by LC-HRMS/ESI (-) for the 22_1866_Rep3 (*green*) and 30_1867_Rep2 (*red*) postage stamps.

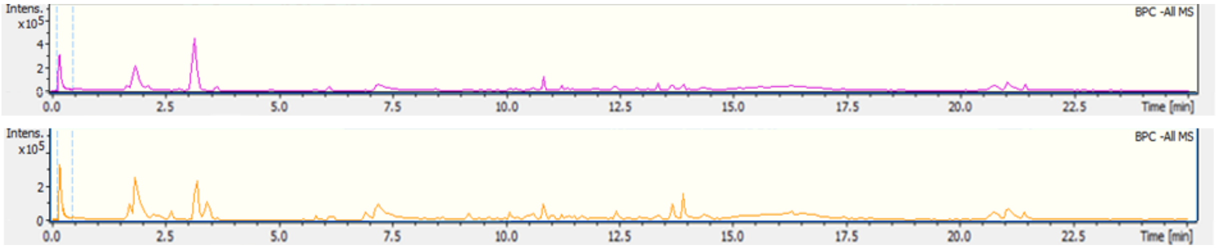


Figure A3.4– Total ion chromatograms obtained by LC-HRMS/ESI (-) for the 40_1870-79_Rep2 (*purple*) and 40_1870-79_Rep3 (*orange*) postage stamps.

Appendix IV – Fluorescence Emission Analysis

The fluorescence emission spectra comparing the postage stamps with the standard are present in the next images (Figure A4.1, Figure A4.2 and Figure A4.3) corresponding to the samples 66_1884_Rep1, 62_1887_Rep1/Rep2 and 160_1909_Rep1/Rep3, respectively.

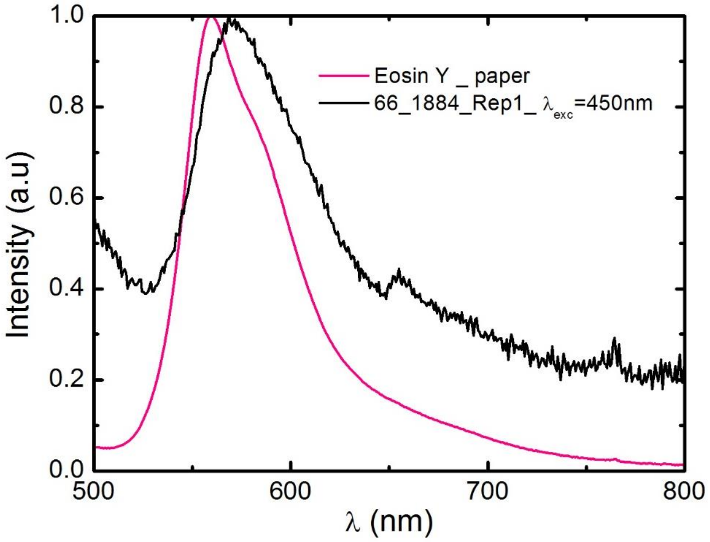


Figure A4.1- Emission spectra comparing the 66_1884_Rep1 postage stamp with the *standard*, eosin y (in paper form – mix of dye in potato starch with water painted in filter paper).

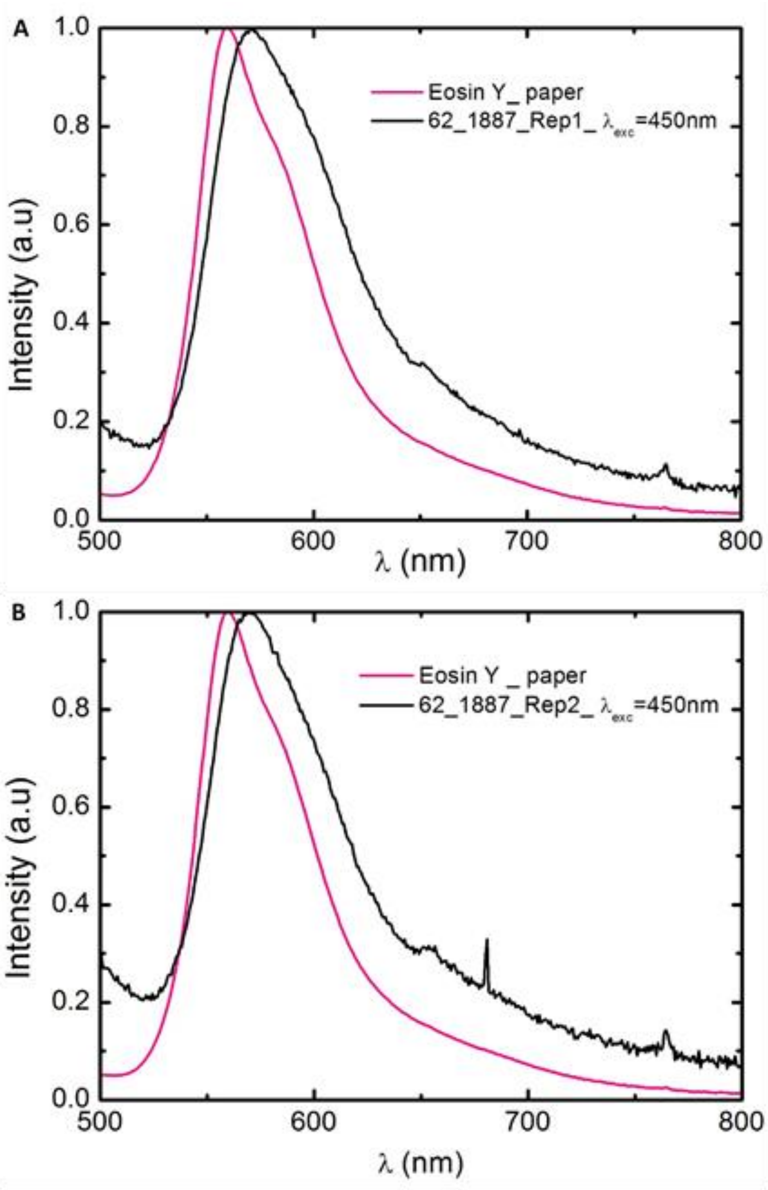


Figure A4.2- Emission spectra comparing the (**A**) 62_1887_Rep1 and (**B**) 62_1887_Rep2 postage stamps with the *standard*, eosin y (in paper form – mix of dye in potato starch with water painted in filter paper).

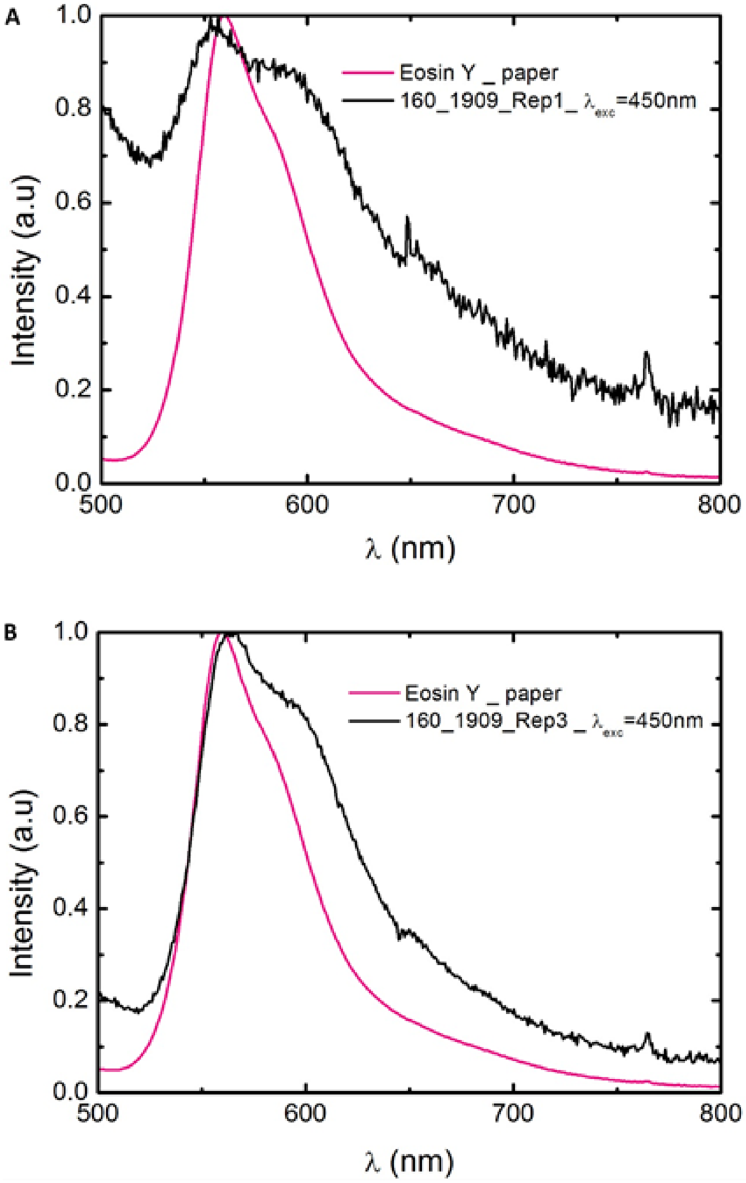


Figure A4.3- Emission spectra comparing the (**A**) 160_1909_Rep1 and (**B**) 160_1909_Rep3 postage stamps with the *standard*, eosin y (in paper form – mix of dye in potato starch with water painted in filter paper).