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Interdisciplinary methods of analysis in museological collections

Revealing Hercule Florence, Friend of the Arts: X-ray Fluorescence Analysis

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ABSTRACT: The debates about Hercule Florence (Nice, France, 1804 - Campinas, SP, 1879) as the pioneer in the discovery of the photographic process were based mainly on his manuscripts, since few of his *épreuves photographiques* (photographic experiments) survived. Technological advances in the last four decades have allowed some of his *impressions à la lumière solaire* to be subjected to analysis by non-destructive techniques at the Instituto de Física of the Universidade de São Paulo in 2016. It was then possible to broaden knowledge of the materials and procedures used in 1833 to obtain the first photographs of the Americas, six years before the announcement of the discovery of the technique by Louis Daguerre in France.

KEYWORDS: Photography. ED-XRF. Analysis of chemical elements. Gold

RESUMO: Os debates sobre o pioneirismo de Hercule Florence (Nice, França, 1804 – Campinas, SP, 1879) na descoberta do processo fotográfico basearam-se, principalmente, em seus manuscritos, uma vez que poucas de suas *épreuves photographiques* (experiências fotográficas) sobreviveram. Os avanços tecnológicos das últimas quatro décadas permitiram que em 2016 alguns destes exemplares de *impressions à la lumière solaire* fossem submetidos a análises por metodologias não destrutivas no Instituto de Física da Universidade de São Paulo. Foi possível, então, ampliar o conhecimento sobre os materiais e os procedimentos utilizados em 1833 para a obtenção das primeiras fotografias das Américas, seis anos antes do anúncio da descoberta da técnica por Louis Daguerre, na França.

PALAVRAS-CHAVES: Fotografia. ED-XRF. Análises de elementos químicos. Ouro

INTRODUCTION

A character with multiple interests and abilities, Antoine Hercule Romuald Florence – or Hercule Florence (Nice, France, 1804 - Campinas, Brazil, 1879) – became known as both a "traveling artist" and an inventor. The most celebrated of his creations was photography, discovered in 1833 when he sought alternative processes for graphic reproduction.

Born in Nice, raised in Monaco (his mother's native country) in a family of artists, imbued with great scientific curiosity and inspired by Daniel Defoe's novel Robinson Crusoe,[4] Hercule Florence joined the French Navy and embarked on the frigate *Marie Thérèse* in 1824 on a journey to circumnavigate the globe.

Having arrived in Brazil at the age of 20, he decided to stay in Rio de Janeiro and soon was hired as the second illustrator of the Langsdorff Expedition. From 1825 to 1829, he traveled more than 13,000 kilometers along the waterways of the Tietê, Paraná, Paraguay, Tapajós rivers and their tributaries (States of São Paulo, Mato Grosso do Sul, Mato Grosso and Pará) before returning to Rio de Janeiro. Hercule Florence wrote the expedition's only complete account – titled "*Viagem Fluvial do Tietê ao Amazonas*" (a river voyage from Tietê to Amazonas) – documenting in text and images the landscape, fauna, flora, people and events along the way.

After the voyage and a stay of a few months in Rio de Janeiro, he settled in the village of São Carlos (now the city of Campinas, SP) - then the most important in the state of São Paulo - and started a family, devoted himself to the management of family businesses (a retail store that sold fabrics, hats and books; Soledad Farm; Florence School), established the first typography of the city and created many inventions.

He recorded his life and work in several manuscripts in French, of which the *L'Ami des Arts livré à lui-même, ou Recherches et découvertes sur différents sujets nouveaux*, written between 1837 and 1859 for publication, constitutes the compendium of his life and work.[5]

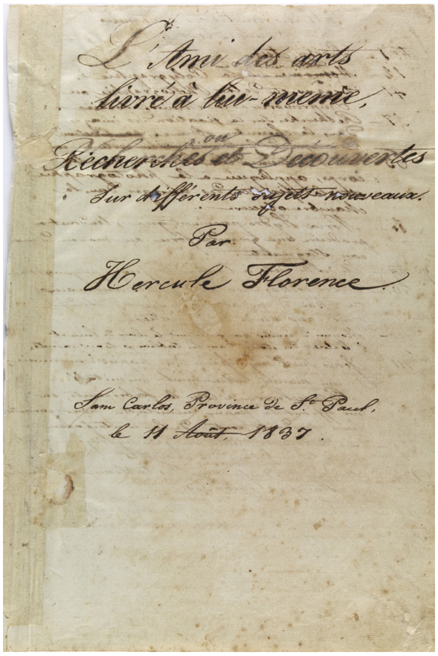
The "*Table des matières*" of this manuscript attests to the breadth of his interests: *polygraphia* (or *autographia*[6]); inimitable paper; photography or printing by sunlight; permanent fixation of *camera obscura* images; stenographic symbols; studies of the sky; research on animal sounds (*zoophony*); a technique to perfectly recreate moonlight and starlight (*tableaux transparents*); a water pump (*nória hidrostática*); the use of hydrogen in aerostats; printing of oil paintings or color prints; hat making (Figure 1).[7]

4. First edition published in London in 1719.

5. The publication (partial and in Portuguese) occurred only in the 1970s, on the occasion of an exhibition at the Museu de Arte de São Paulo, cf. Florence (1977). In 2018 the complete facsimile was published, accompanied by diplomatic transcription by Thierry Thomas, cf. Florence (2015). A new Portuguese translation is in preparation, illustrated with drawings and watercolors preserved in the Bibliothèque National de France (Paris), in the Archives of the Russian Academy of Sciences (St. Petersburg) and in the IHF.

6. Polygraphy (or autography) was Hercule Florence's first major invention related to printing. It was conceived in 1831, when the artist sought alternatives for the publication of his article on zoophony (record of "animal voices"). In opposition to the laborious and costly techniques of typography and lithography, he proposed the use of a wax plate as a matrix and a denser ink. This allowed him to print without the need for a large, heavy press. After some years of experiments (conducted in parallel with his research on photography), Hercule Florence came to the simultaneous printing of all colors, which meant a huge technical advance over traditional engraving and led him to develop the inimitable paper. Although applied to small commercial forms (pharmacy labels, advertising), polygraphy was never marketed.

7. "Un assez grand nombre de matières, parmi lesquelles il en est qui n'ont pas le moindre rapport



L'Ami des arts
livré à lui-même,
ou
Recherches et Découvertes
sur différents sujets nouveaux.
Par
Hercule Florence

San Carlos, Province de St Paul,
le 11 Août 1837.

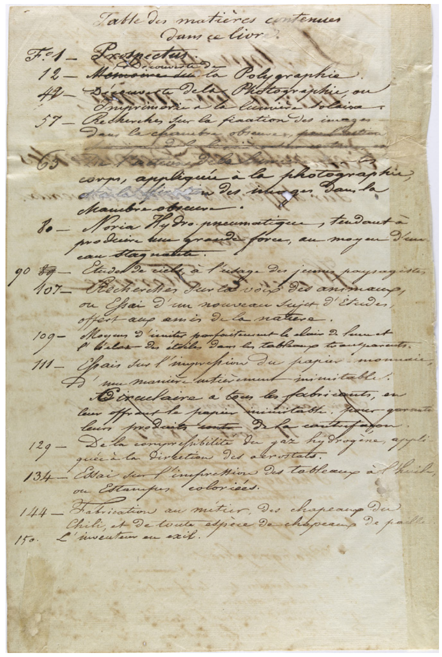


Figure 1 - Hercule Florence. Title sheet and summary of the manuscript *L'Ami des arts...*, 1837-1859. Iron gall ink on paper, 30.6 x 21.0 cm. Instituto Hercule Florence Collection (São Paulo). Photo: Heitor Florence

Almost a hundred years after the death of the artist-inventor, his researches began to be reappraised - especially those concerning the development of photography. Thanks to his great-grandson Arnaldo Machado Florence (1911-1987) and Professor Boris Kossoy (1941), it was possible to recover the procedures performed by Hercule Florence in the 1830s to develop the technique that he would call *photographie* or *imprimerie a la lumière solaire.*[8]

Since 2009 the archives documenting the efforts to recognize Hercule Florence as one of the world's pioneers of photography, together with six manuscripts written between 1829 and 1863,[9] are in the keep of the Instituto Hercule Florence (IHF), an institution founded in 2006 by his great-great-grandson Antonio Florence.

In June 2016, IHF acquired a precious collection: the *Polygraphie* and *Photographie* series of quill pen drawings that were originally part of the *L'Ami des Arts...* manuscript; a drawing for a Masonic diploma made with quill pen

entre elles, va être traité dans cet ouvrage: tant d'entreprises diverses ne sont guères (sic) propres à me gagner une opinion favorable, mais je prie le lecteur de remarquer que parmi les articles qui vont suivre, six ont du rapport à la peinture: j'observe aussi que presque toutes mes recherches et découvertes, sont nées de circonstances où je me suis trouvé." (*L'Ami des arts...*, p. 1)

8. For this pioneering work, cf. Kossoy (2006).

9. They are: *L'Ami des Arts...* (1837-1859); *Livre d'annotations et de premiers matériaux* (1829-1834); *2e livre de premiers matériaux* (1834-1840, except for a later note dated 1859); *Troisième livre de premiers matériaux* (1840); *L'inventeur au Brésil. Correspondances et pièces scientifiques* (1862-1863); e *Ensaios de Pintura Solar e de Pintura Cisparente* (1862). Coming from the Arnaldo Machado Florence Collection and preserved by his daughter Teresa Cristina Florence Goedhart, at the IHF the manuscripts were stabilized by Patricia Giordano, digitized in high resolution (with Hasselblad H2 camera with Phaseone P45 digital back) by Heitor Florence and transcribed (diplomatically) by historian Thierry Thomas.

and graphite; and two *impressions à la lumière solaire* ("sunlight printings": a Masonic diploma and a series of nine pharmacy labels).[10]

These items, formerly belonging to the Arnaldo Machado Florence Collection, had been missing since September 1989.[11] Their whereabouts remained unknown for 27 years until they were found by family members and transferred to IHF.[12]

Following the items' identification, stabilization and storage, the IHF and the Research Center for Physics Applied to Artistic and Historical Heritage (NAP-FAEPAH) of the Instituto de Física of the Universidade de São Paulo (IFUSP) resumed their partnership[13] to perform physical and chemical non-destructive analyses of the two *impressions à la lumière solaire*, in an attempt to recover the procedures performed by Hercule Florence with the support of a friend, the chemist and botanist Joaquim Corrêa de Mello (1816-1877).

The main goal of the initial analyses was to identify the chemical elements and investigate the production of works with such distinct characteristics, despite mentions in the manuscripts that a photographic process was involved in the production of both printings. While the *Masonic Diploma* presents a very faint and barely visible image[14], the *Pharmacy Labels* show a darker (or permanent) imprint on a paper marked with violet spots.[15]

In addition to contributing to recover Hercule Florence's work methodology and pioneering in the development of photographic techniques, determining the chemical elements present is essential for making decisions regarding the storage, handling and possible exposition of the works, ensuring their physical long-term preservation.

Individual physicochemical characteristics make each work react differently to light, heat, humidity and pollution, requiring specific conditions to prevent deterioration and irreversible loss of content - especially for images still prone to suffer alterations, and in the case of an inventor like Hercule Florence, who experimented with various substances and processes to achieve his goal of multiplying and fixing his records.

The physical preservation of the items was also a criterion for selecting the analytical techniques employed, which must be non-destructive: energy dispersive X-ray fluorescence (ED-XRF), which allows the determination of the elemental composition of the materials, and observation with a stereomicroscope, which enables a three-dimensional digital reconstitution of the object through the combination of two-dimensional images.

Portable Raman spectroscopy analysis was also proposed, which would allow the identification of the items' chemical compounds without the need for

10. Kossoy (2006, p. 204-215).

11. Kossoy (2006, p. 204). See also Teresa Cristina Florence Goedhart's correspondence with Boris Kossoy, dated May 18, 1999. Available at: <https://bit.ly/2wYvZrU>. Accessed on: Sep 17. 2016

12. The Instituto Hercule Florence (IHF) has a specialized collection, library and archives (Fundos Arnaldo Machado Florence, Dr. Érico João Siriuba Stickel, Dr. Rosemarie Erika Horch, Prof. Ana Maria Camargo/ Rubens Borba de Moraes and Florence Family). However, its activities are conducted mainly through partnerships with other museological and research institutions, aiming at the localization, cataloging, digitalization and availability of documents and images related to the life and work of Hercule Florence, the scientific and cultural production resulting from the Langsdorff Expedition and the history and iconography of the 19th century Brazil. The various ongoing projects, items from their own collection and from partner institutions can be found at <www.ihf19.org.br>.

13. Instituto Hercule Florence, NAP-FAEPAH and Museu Paulista of the Universidade de São Paulo signed in 2014 a partnership to digitalize, using an Osiris infrared camera, the notebook of the artist Aimé Adrien Taunay (1803-1828). Underneath the records visible with the naked eye (most of them done in iron gall ink) were revealed pencil annotations describing aspects of Taunay's stay in Rio de

Janeiro before joining the Langsdorff Expedition.

14. The work bears the following inscription in Hercule Florence's own calligraphy: "Celui-ci n'a été que peu desoxidé; voila le motif de sa páleur (sic) et décoloration en plusieurs endroits. Photographié en 1832, sept ans avant que j'eusse la 1.e notion que d'autres faisaient les mêmes recherches avec plus de succès." Hercule Florence was probably mistaken in dating the photograph to 1832; in his manuscripts, the first experiments with sunlight printing date back to January 1833.

15. Photoprinted on bottom edge of the paper, mirrored: "Photographia by H. Florence, inventor of Photographia" and "H. Florence, del. et sculp." (abbreviations of "delinavit et sculpsit," terms borrowed from the engraving process to indicate the designer and engraver).

16. In addition to the IHF team, the research involved independent professionals from the fields of Physics, Photography, History of Photography and Museum Preservation, as well as Linda Fregni, curator of the exhibition *Hercule Florence, Le Nouveau Robinson* (Nouveau Musée National de Monaco, March-September 2017).

special preparation or removal of samples. However, this technique uses a small low-power laser source - although exposure would be brief, in this particular study (where objects are probably still photosensitive) there was a risk of irreversible damage. Thus, this possibility of damage was determinant for portable Raman spectroscopy not to be applied particularly in this case.

All of these analyses were conducted in September and October 2016, with constant debate among the multidisciplinary research team.[16] This article presents the results obtained.

ANALYZED OBJECTS

Three original works produced by Hercule Florence in the 1830s, currently belonging to the Instituto Hercule Florence Collection (São Paulo), were analyzed:

* i*mpression à la lumière solaire* "Pharmacy labels" (Figure 2)
* *impression à la lumière solaire* "Masonic Diploma" (Figure 3)
* "inimitable paper" executed in polygraphy (Figure 4)

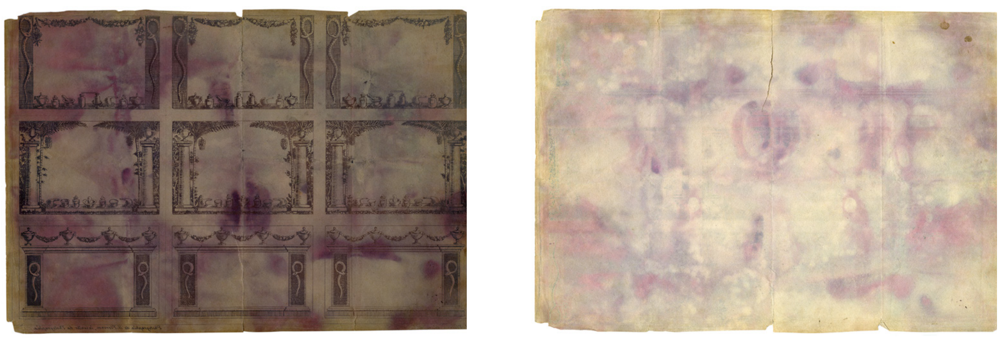


Figure 2 - Hercule Florence. [*Pharmacy labels*, front and back], [1833-1839]. Photographic copy of pharmacy labels, obtained on photosensitive paper by contact under sunlight, 21.0 x 29.4 cm (irregular). Instituto Hercule Florence Collection (São Paulo). Photos: © Studio 17 - Patricia Filippi and Millard Schisler

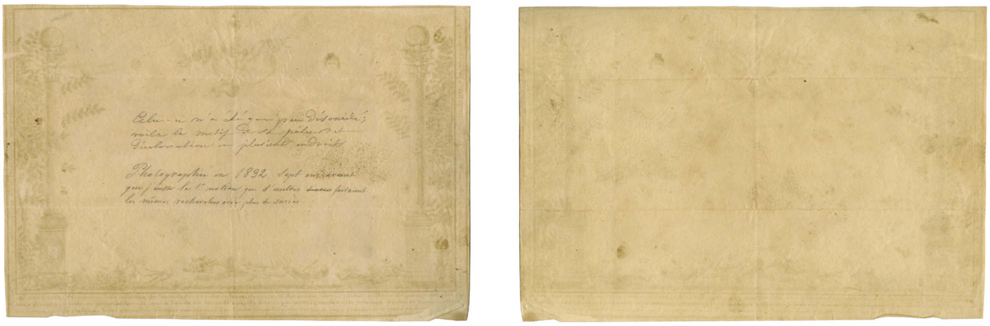


Figure 3 - Hercule Florence. [*Masonic diploma*, front and back], [1833-1839]. Photographic copy on photosensitive paper, obtained by contact under sunlight, 20.2 x 29.1 cm (irregular). Instituto Hercule Florence Collection (São Paulo). Photos: © Studio 17 - Patricia Filippi and Millard Schisler

Figure 4 - Hercule Florence. [*Inimitable paper*] after 1838.[17] Polygraphic ink on paper, 13.7 x 21.8 cm. Instituto Hercule Florence Collection (São Paulo). Photo: © Heitor Florence

17. The first mention of the inimitable paper is recorded in *L'ami des arts*... (p. 111-127) dated November 25, 1838. Its use as paper money is suggested in the *2e livre*... (p. 60, undated).

ANALYTICAL TECHNIQUE

Energy Dispersive X-Ray Fluorescence (ED-XRF) is a non-destructive analytical technique that has been widely used to investigate chemical elements in cultural heritage items. It is a very effective method for the identification of the chemical elements present in the different supports (paper, canvas, fabric etc.) and in the superimposed layers (mainly inorganic material such as pigments, photosensitive substances, fixatives etc.).

X-ray Fluorescence - Experimental Section

A portable X-ray fluorescence system consisting of an Amptek® silver filament X-ray tube system (30 kV and 10 μA) and an Amptek® Si-Drift detector were also used for analysis from (Figure 5, left: Ag tube); and a system consisting of an Amptek® gold-plated X-ray tube (30 kV and 5 μA) and an Amptek® Si-Drift detector (Figure 5, right: Au tube).[18]

During measurements, the ED-XRF system is positioned close to the object without touching it and causing no damage of any kind.[19] Each measurement takes 100 seconds and covers an area of approximately 3 mm in diameter. The measurement distinguishes the main elements and any impurities that may be present - this fact, often undesirable, can be advantageously used as a digital mark of the artist's procedures or of the environment in which the work was created.[20]

These two X-ray systems with different kinds of tubes - silver (Ag) and gold (Au) - were used in order to confirm the possible identification of these elements in the analyzed objects and to discard interferences of the X-ray beams of both tubes.

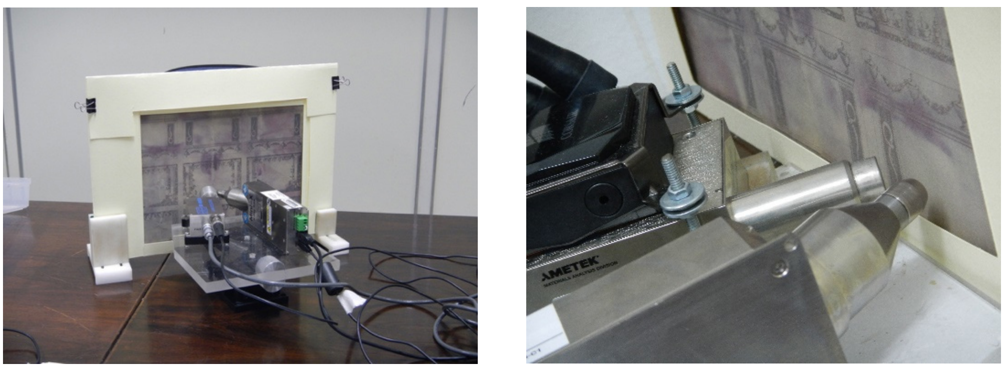


Figure 5 - Images of measurements being made with portable XRF systems used in the analyses at USP - IFUSP Institute of Physics (left, Ag tube) and the IPEN Energy and Nuclear Research Institute (right, Au tube). Item *Pharmacy Labels*, IHF Collection. Photo: the authors.

18. Portable gold tube fluorescence system belonging to Professor Cibele Zamboni (IPEN-SP).

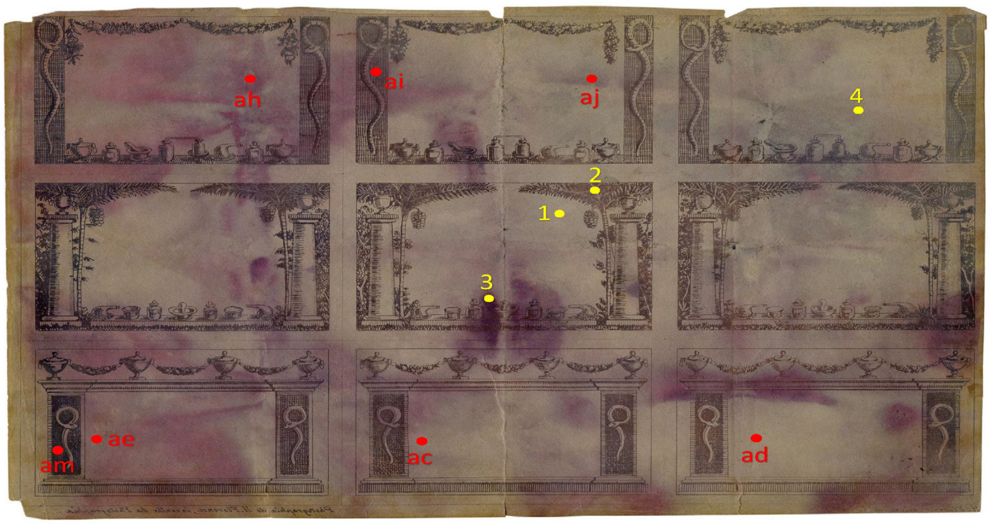
19. During measurements, the ED-XRF (energy dispersive) system is positioned a short distance from the stand-mounted work (with no back support) and placed upright. This assembly allows the results to be limited to the work itself, without interference from substances other than air.

20. ED-XRF is indicated for detection of elements with atomic number greater than 12 (magnesium Mg) and less than 92 (uranium U). Carbon (C), nitrogen (N) and oxygen (O), which have an atomic number lower than 12, are not detectable.

RESULTS OF ED-XRF MEASUREMENTS

Item: *Impression à la Lumière Solaire (Pharmacy Labels)*

ED-XRF analysis investigated different points in the work *Pharmacy Labels* to identify the chemical elements present in the different areas, both the light and the violet and dark ones. Figure 6 shows the location of the points selected for the measurements, with both the Ag tube (points *1* to *4*) and the Au tube (points *ac* to *am*).



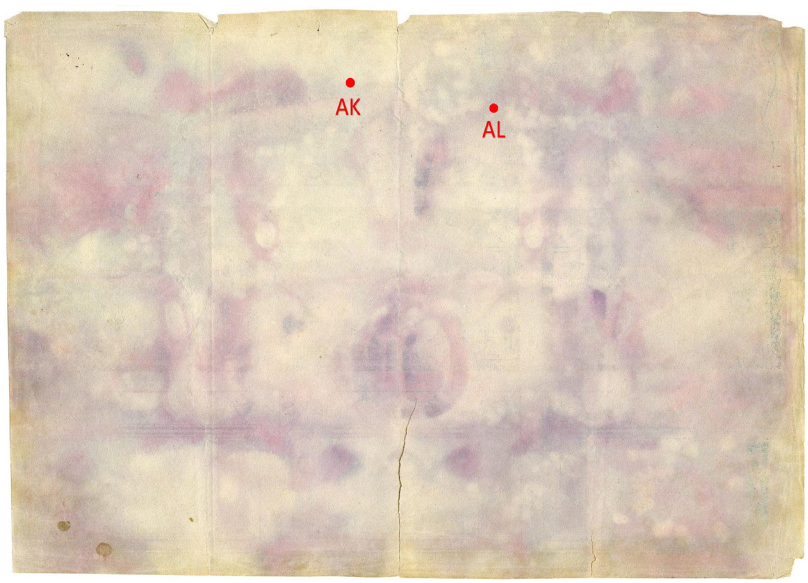


Figure 6 - Map of the distribution of the points examined in the item "*Pharmacy Labels*" of the IHF Collection, front and back. Points 1 to 4 analyzed with IFUSP's portable XRF system (Ag tube); points *ac* to *am* analyzed with IPEN's portable XRF system (Au tube).

Table 1 identifies and details each measured point in *Pharmacy Labels* and Figure 7 shows the ED-XRF spectra obtained for some of the measured points and the respective chemical elements identified.

Table 1_ Nomenclature and specification of points measured by ED-XRF on item *Pharmacy labels*

REFERENCE	NOMENCLATURE	DESCRIPTION
		Ag Tube – IFUSP
160909ad	1	Center label - Light Area, no image
160909ae	2	Center label - Image
160909af	3	Center label - Very dark violet spot
160909ag	4	Top right label - Area darker than 1, no image
		Au Tube– IPEN
160916ac	ac	Bottom center label - Area without image, with light violet spot
160916ad	ad	Bottom right label - Area without image and without spot
160916ae	ae	Bottom left label - Area without image with dark violet spot
160916ah	ah	Top left label - Area without image, with violet spot
160916ai	ai	Center top label - Image area
160916aj	aj	Top center label - Area without image and without spot
160916ak	ak	Back side - Top margin - Light area
160916al	al	Back Side - Top margin - Dark Area
160916am	am	Bottom left label - Dark image area

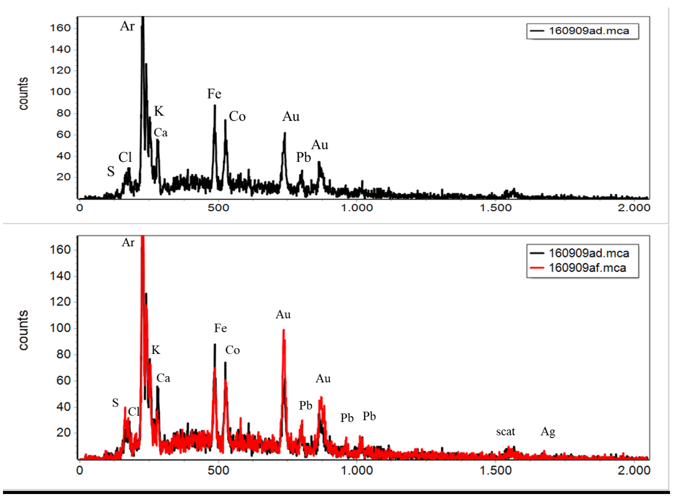


Figure 7 - ED-XRF spectra from item *Pharmacy labels*. Top: Measurements of point P1, located in a clear area of paper, with no image. Bottom: Comparison of measurements in the light area of the paper, without image (the same P1, with spectrum in black), and in the dark violet spot located in the central area of the support (P3, with spectrum in red) (Ag tube - IFUSP).

The analyses of the spectra in Figure 7 show the chemical elements sulfur (S), chlorine (Cl), potassium (K), calcium (Ca), iron (Fe), cobalt (Co), gold (Au) and lead (Pb). The element argon (Ar) corresponds to the air excited during the measurements. The broad peak found at the end of the spectrum and identified as "Scat" refers to the scattering of the silver X-ray beam (Ag) in the sample.

The small silver peak (Ag) could be unrelated to materials present in the work, but derive instead from interference from the silver tube itself used in this measurement. For this reason, measurements were also performed with a gold X-ray tube (Au) belonging to the IPEN (Institute for Nuclear Energy Research), to more clearly ascertain whether the chemical element silver (Ag) is present in this work.

Gold (Au) is clearly identified in these spectra, suggesting the use of composite materials containing gold (Au), such as the gold nitro-hydrochloride mentioned in Hercule Florence's manuscripts. We can observe that the amount of gold (Au) present in the area related to the gold peak identified in the spectrum of Figure 7 (red line) is higher in the violet colored point, which may indicate a larger amount of this material.

Cobalt (Co) may also be related to the observed blue/violet coloration, which could come from contact with cobalt violet or cobalt blue pigments.

Iron (Fe) may also be related to Prussian blue - both pigments may have contaminated the work or been used at some point by the artist.

The potassium (K) identified in the spectra may also be related to the use of potassium hydroxide as reported by Florence in his notes.

The element lead (Pb) is present in smaller quantities and may show contamination during the artist's preparation of his own materials.

To confirm the existence or not of silver (Ag) in this work, we chose to use a gold-tube ED-XRF system (Au). Figure 8 shows a typical spectrum of the ED-XRF system obtained with the gold tube (Au) and the respective chemical elements identified in a point inside a stain (point ah) in *Pharmacy Labels*.

We can clearly observe in the spectrum shown in Figure 8 the same elements identified with the silver tube (Figure 7). In the figure above, the region marked with the circle shows that there is no trace of silver (Ag), confirming that there is no silver present in this work - and that it does contain gold.

This kind of measurement is best taken without using silver- or gold-filament X-ray tubes, but they are often not readily available (portable equipment dedicated to heritage studies). In the future, we suggest that these measurements should be repeated using an X-ray tube of another material. However, by comparing both tubes' measurements, it became evident that this work contains gold, not silver.

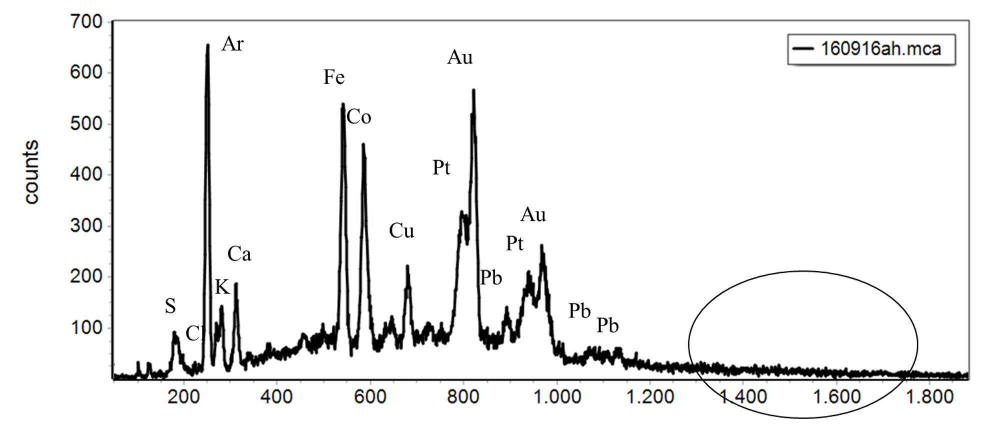


Figure 8 - ED-XRF spectrum of item *Pharmacy labels* for point ah (label in the upper left corner of the paper, area with violet spot). The area highlighted with a circle shows that there is no silver peak (Ag) (Au tube - IPEN).

Similar to previous measurements, the element argon (Ar) refers to air, and copper (Cu) and platinum (Pt) are related to the experimental arrangement, not to the work itself.

The systematization of the data obtained by the ED-XRF technique for *Pharmacy Labels*, relating the area of the peaks found in the spectra (X-ray of the measured elements) at each point and for each identified chemical element, can be visualized in the bar charts of Figure 9.

The results show that the light spots contain a higher amount of potassium (K) (according to Florence's notes, this may be related to potassium hydroxide). Stained and dark spots contain a high amount of iron (Fe) and cobalt (Co), which could indicate contact with pigments that have these chemical elements in their composition (for example, cobalt violet and Prussian blue or cobalt blue).

The analysis of the bar chart for gold (Au) shows a relationship between the largest area of the Au peak and the dark points on the drawing - that is, the points measured in the darkest areas contain a larger amount of gold (Au), suggesting higher fixation of this element at these points. A similar relationship applies to iron (Fe). The amount of lead (Pb) is low in all measured points, making it difficult to explain its use in this photographic work. As mentioned earlier, this could be related to the artist's procedures or to contamination in the preparation of paint or other materials.

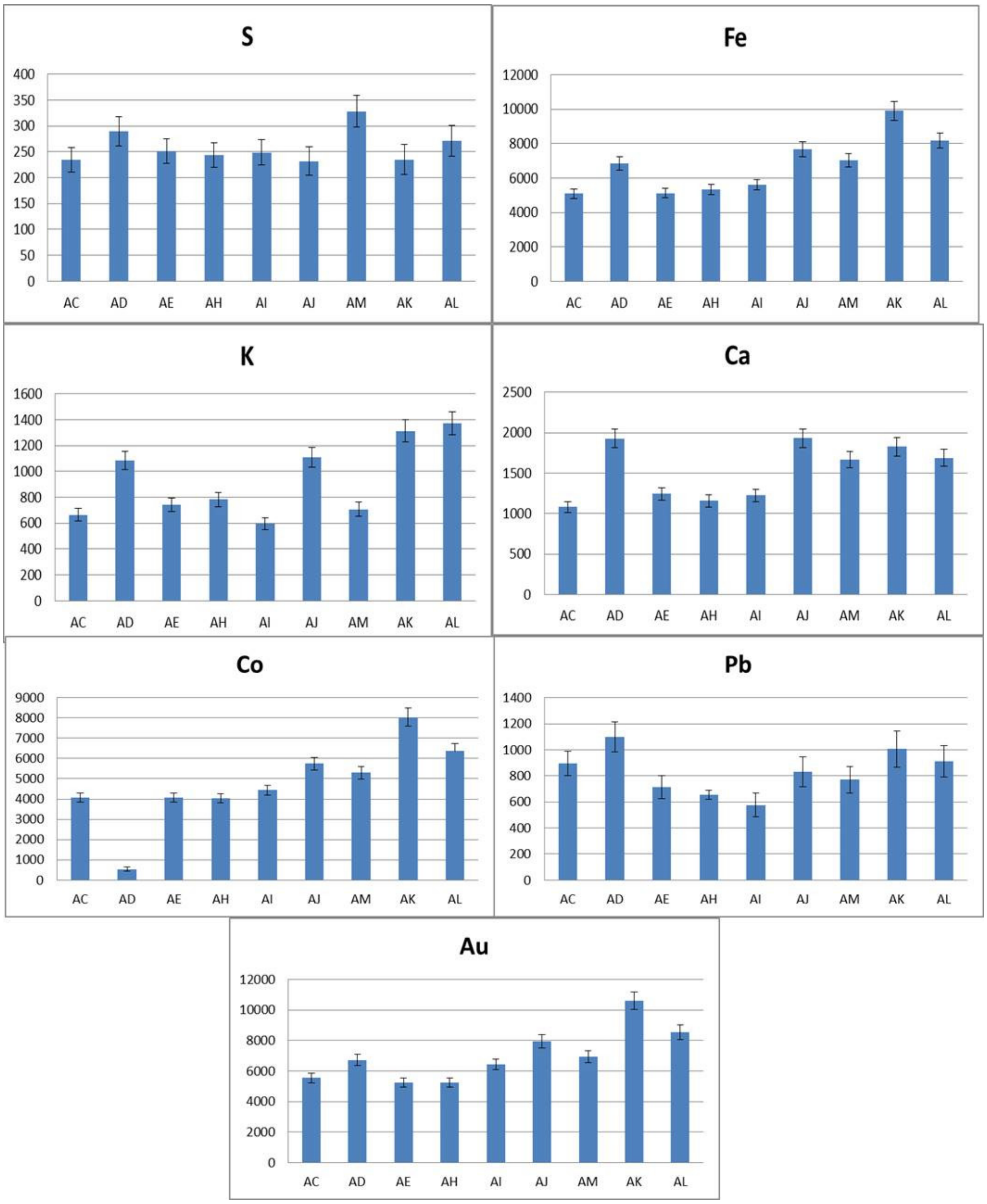


Figure 9 - Bar charts of areas calculated for the chemical element peaks identified in the XRF spectra for the different points of the item *Pharmacy labels*: sulfur (S), potassium (K), calcium (Ca), iron (Fe), cobalt (Co), lead (Pb) and gold (Au). Note that the charts are in different scales for better visualization (gold tube - IPEN).

Another important result of bar graphs' analysis is also related to the area (concentration) of the elements potassium (K), iron (Fe), cobalt (Co) and gold (Au), which is larger at points ak and al located at the backside of the paper not corresponding to dark spots on the front. One hypothesis for this result may be the method used by Hercule Florence and Joaquim Corrêa de Mello to sensitize and/ or fixate the image by immersing the paper in a solution. The reverse side of this copy, therefore, would have come in contact with a slightly larger – but detectable using ED-XRF – amount of such chemical elements.[21]

Another hypothesis related to potassium (K) and calcium (Ca) may be the use of urine in the fixative solution – which could be the origin of these elements. In the manuscript Livre d'annotations, Florence mentions the use of urine on April 8, 1833, during an experiment with gold salts.[22] The same association "gold-urine" appears in L'ami des arts.[23] As for silver, Florence does the opposite: he recommends that urine should not be used in experiments with silver nitrate.[24]

The calcium (Ca) identified at all measured points may be related to paper manufacture. Lead (Pb), on the other hand, could be due to traces of the white lead used by Hercule Florence to transfer the contours of the drawing to the glass plate that served as the image plate.

The origin of cobalt (Co), however, remains doubtful, as it may be related to some pigment, photosensitizing solution, fixative solution, or to some kind of contamination occurring in the making process or storage of *Pharmacy Labels* along its more than 175 years of existence. Thus, further research should decipher the origin of the elements identified.

Item: *Impression à la Lumière Solaire* (Masonic Diploma)

For this work we also used the ED-XRF system with both gold and silver tubes, and different points on the front and back were investigated. Again the goal of these analyses was to identify the chemical elements present in the different light and dark regions. Table 2 and Figure 10 show the identification and position of the points measured by the ED-XRF technique.

21. In *L'Ami des Arts*..., Hercule Florence registers his recommendations for the application of the photosensitive solution: "Comme le chlorure noircit ou se ternit par l'effet de la lumière du jour, on doit mouiller le papier le soir, ou pendant le jour, mais dans une chambre presque obscure. **On trempe le pinceau dans le chlorure** [d'or], et **on mouille une seule face du papier**" (p. 47). The following page describes the procedure for image fixation: "on le porte à l'obscurité, **on le met dans un bassin où il y a de l'eau et de l'urine**; le dessin devient immédiatement noir par l'action de l'urine; on l'y laisse assez de temps, et quand on le retire, on le fait sécher à l'ombre."

22. *Livre d'annotations*... p. 141bisv, 142bisv. The nomenclature "bis" was adopted in cases where Hercule Florence was mistaken, using twice the same page numbers. The "v" indicates the back of page 141bis.

23. *L'Ami des Arts*... p. 48-49, 74.

24. *Livre d'annotations*... p. 51.

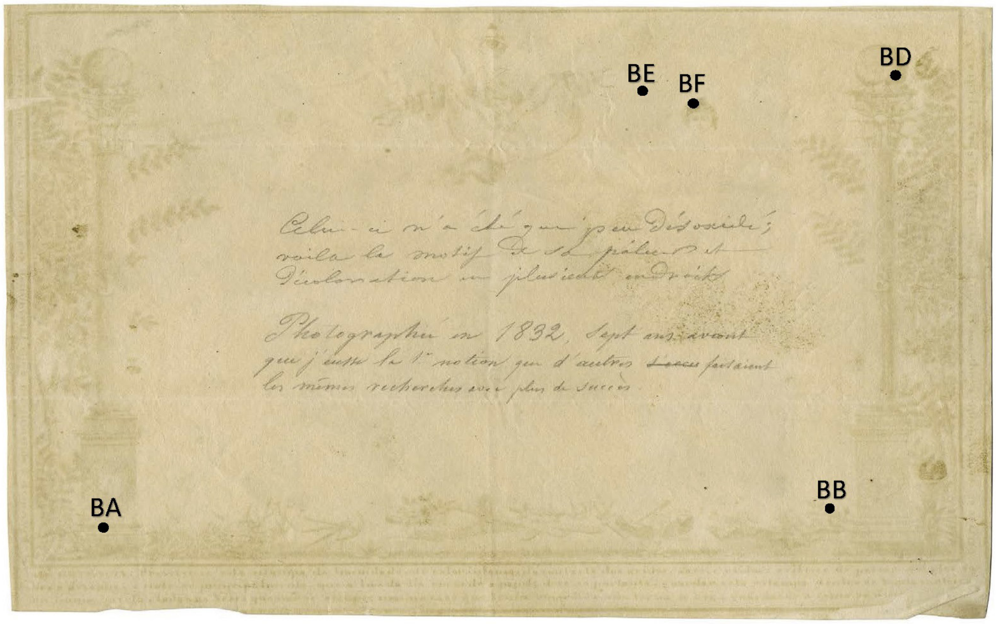
Table 2_ Nomenclature and specification of points measured by XRF in item *Masonic Diploma*

REFERENCE	NOMENCLATURE	DESCRIPTION
		Au tube– IPEN
160916ba	BA	Lower left - Dark point - P1
160916bb	BB	Lower right - Lighter point - P2
160916bc	BC	Back side - Bottom margin - P3
160916bd	BD	Upper right - Drawing point - P4
160916be	BE	Upper margin - Clear point between angel and angel group
160916bf	BF	Upper margin - Image (dark point in angel figure)
160916bg	BG	Back side - Top margin - Light area
		Ag tube– IFUSP
161013ba	Ba	Lower left - Dark point - P1
161013bb	Bb	Lower right - Lighter point - P2
161013bc	Bc	Back side - Bottom margin - P3
161013bd	Bd	Upper right - Point in drawing - P4
161013be	Be	Clear point between angel and group of angels - P5
161013bf	Bf	Dark point in angel drawing - P6
161013bg	Bg	Clean back side - P7
161013bh	Bh	Point near bottom right - Dark drawing area
161013bi	Bi	Lower right quadrant - Light area without image and without spot

Figure 11 shows a typical ED-XRF spectrum obtained from the *Masonic Diploma* for a bright spot (point *bb*, located in the lower right corner). Neither gold (Au) nor silver (Ag) was detected in this work, but only sulfur (S), chlorine (Cl), potassium (K), calcium (Ca), iron (Fe), copper (Cu), arsenic (As) and lead (Pb), which show very low peak counts, suggesting low concentrations of these elements. In addition to the expected elements and spectra, copper (Cu) and arsenic (As) were also detected on both sides of the paper, perhaps of environmental origin.[25]

When comparing the ED-XRF measurements of the *Masonic Diploma* and *Pharmacy Label* works (Figure 12), it is clear that the amount of the chemical elements present in the former is much smaller compared with the latter. The non-detection of gold (Au) or silver (Ag) in the Masonic Diploma may be due to the small amount of these elements and/or to the detection limit of the technique (which makes their presence doubtful).

25. Arsenic appears in Hercule Florence's reading notes of July 1833: cf. *Livre d'annotations...* p. 148 ("acid arsenique") and p. 148v ("acide arsénieux"). The same reference to the research of Antoine François, Count of Fourcroy (1755-1809), is repeated in *L'ami des Arts...* (p. 77). Its presence, like that of copper, could be explained by the pigments used by Hercule Florence in other experiments.



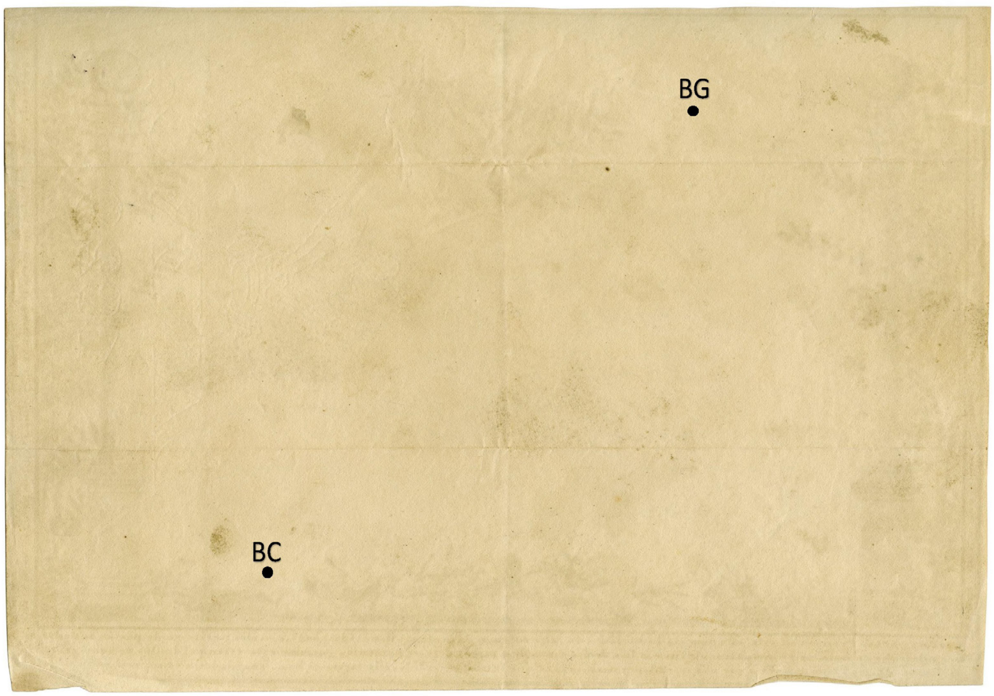


Figure 10 - Map of the distribution of points examined in item *Masonic diploma* (front and back) with the portable ED-XRF systems from IFUSP (Ag silver tube) and IPEN (Au gold tube).

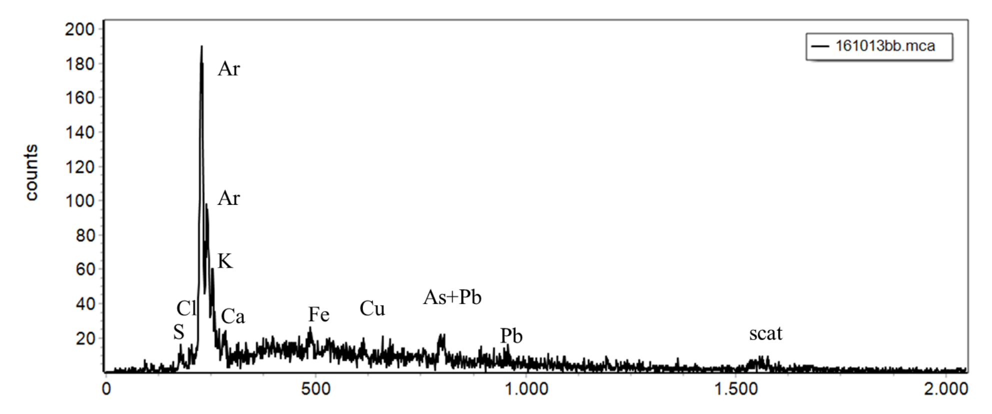


Figure 11 - ED-XRF Spectrum of item *Masonic diploma* for point *bb* (light spot located in the lower right) (Ag tube).

While the *Pharmacy Labels* photograph shows marked traces of cobalt (Co), in the impression of the diploma the amount found of this element is zero (or practically zero).

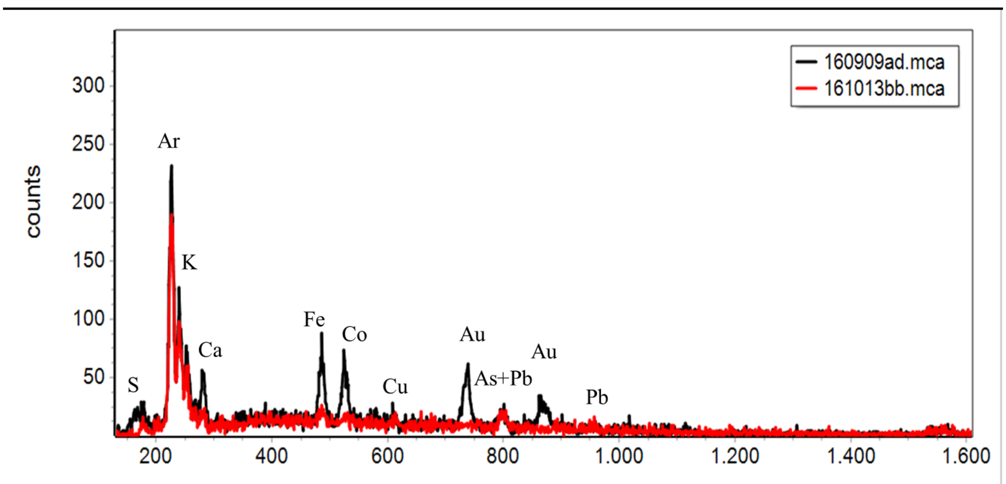


Figure 12 - Two XRF spectra comparing measurements in clear, non-image areas of items *Pharmacy labels* (point 1, spectrum in black) and *Masonic diploma* (point bb/P2, in red) obtained with the portable Ag tube system (IFUSP).

The differences between the two works can be explained by differences in the chemical compositions of the paper and in the photosensitive and fixative solutions used in each case. The most obvious would be to suppose that in the *impression à la lumière* of the *Masonic Diploma* used much more diluted solutions (i.e. with low concentration or absence of chemical elements). This would also explain the attenuated, barely visible image, either for lack of photosensitive substances or for lack of fixative substances - in contrast to the *Pharmacy Labels*.

However, the cause of the faintness of the image cannot be confirmed: experimental processes, improper storage, exposure to moisture, deterioration and other factors brought on by time, alone or in combination, can yield similar results. Measurement results for points in light and dark regions were systematized in bar graphs that allow us to identify variations in the amount of a given chemical element at the various points (Figure 13). As an example of this type of analysis, greater variation of calcium (Ca) presence can be observed for measured points in the dark regions. Statistically, for most elements - for example, iron (Fe) and potassium (K) - it was not possible to state which ones correlate with the darker or lighter regions.

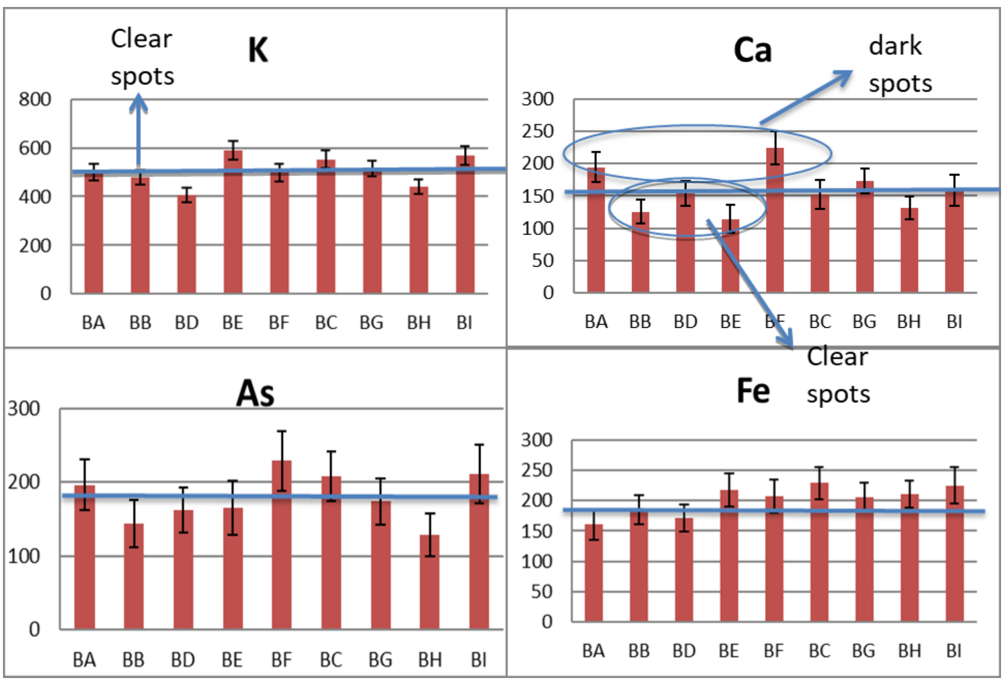


Figure 13 - Bar chart for the elements potassium (K), calcium (Ca), arsenic (As) and iron (Fe) obtained from the peak areas of the ED-XRF spectra of item *Masonic diploma*, measured at the various points with Ag tube. Note that the charts have different scales for better viewing.

The elemental analyses performed so far on the two *impressions à la lumière solaire* belonging to the IHF collection correspond to Hercule Florence's descriptions of experiments with photosensitive elements alternative to silver. If in the *Pharmacy Labels* the element seems to be gold (Au), in the *Masonic Diploma* doubts remain. However, as stated above, the non-detection of gold (Au) or silver (Ag) in the *Masonic Diploma* may be due to the reduced amount of these elements and/or to the detection limit of the technique.

If we follow Boris Kossoy's studies, the same characteristics are probably to be found in the items (or samples) preserved in the Cyrillo Hercule Florence (São Paulo) and Instituto Moreira Salles (Rio de Janeiro) collections.[26]

Scientific researches using other techniques, combined with consultation with other documents left by Hercule Florence, and historical research on the availability, application and practices associated with certain chemicals in nineteenth-century Brazil may provide new information and contribute to the understanding of current results.

26. Kossoy (2006, p. 215-220).

27. *L'ami des arts...*, p. 111-127.

Item: *Inimitable Paper* Polygraphy

For comparison purposes, we extended ED-XRF analyses to a copy of the inimitable paper developed by Hercule Florence for a new Brazilian monetary system.

Applicable at both local and national levels, the inimitable paper would be the basis for a single currency, countering the regional or worthless emissions that began to proliferate in the Brazilian economy in the 1840s.

The process for producing the inimitable paper was the same as that for polygraphy (thus not involving photosensitization, but a technique for engraving and printing several colors simultaneously). Several polygraphic inks (created by Hercule Florence and denser than those used in ordinary printing) were placed in a container and mixed partly and randomly with a heated metal tip. Thus were created unique designs and tones, on which was pressed a sheet of paper. The slight humidity caused the inks to be absorbed by the paper, and the strokes and colors were permanently imprinted. Reproducing the combinations of shapes and colors was virtually impossible - which, according to Hercules Florence, would protect the issuer from illegal counterfeiting.[27]

In the inimitable paper analyzed by NAP-FAEPAH, the colors green, yellow and pink predominated. In measurements with the portable ED-XRF system (Ag tube), two areas of each of these colors were analyzed, plus an CA point on the unprinted margin of the paper. The different measured colors are identified in Figure 14 and Table 3.

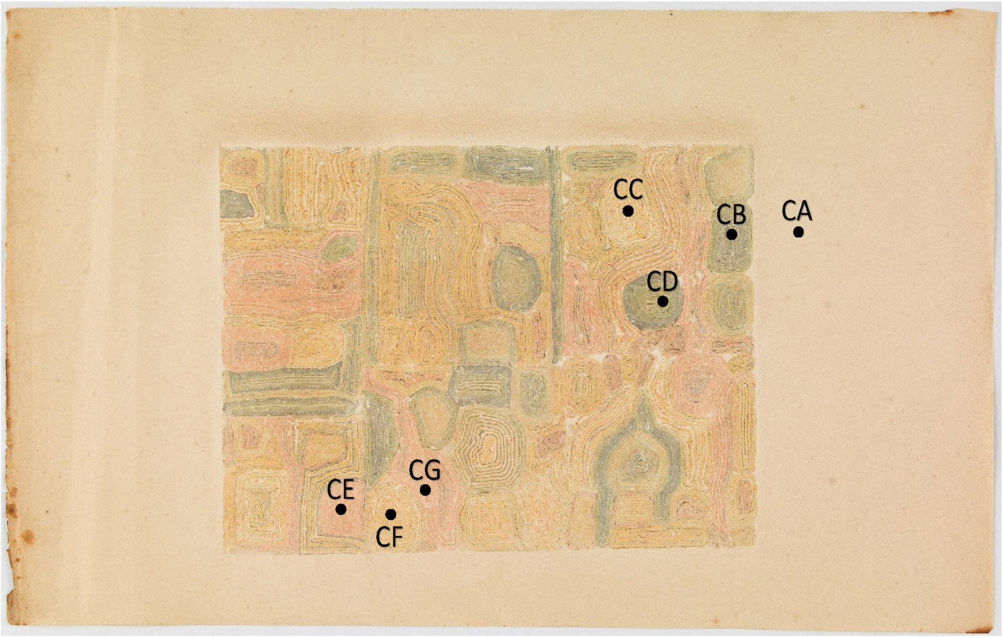


Figure 14 - Distribution map of points *CA* to *CG*, measured on item *Inimitable paper* of the IHF Collection, analyzed with IFUSP's ED-XRF portable system (Ag tube).

Table 3_ Nomenclature of points measured by ED-XRF in item *Inimitable Paper*

CA	CB	CC	CD	CE	CF	CG
Paper	Green	Yellow	Green	Pink	Yellow	Pink

Figure 15 shows the ED-XRF spectra obtained for the *Inimitable Paper* in the green, yellow and pink pigmentation areas. The elements sulfur (S), potassium (K), calcium (Ca), iron (Fe), mercury (Hg) and lead (Pb) were observed.

The bar charts in Figure 16 allow a better identification of the main elements for each pigmentation:

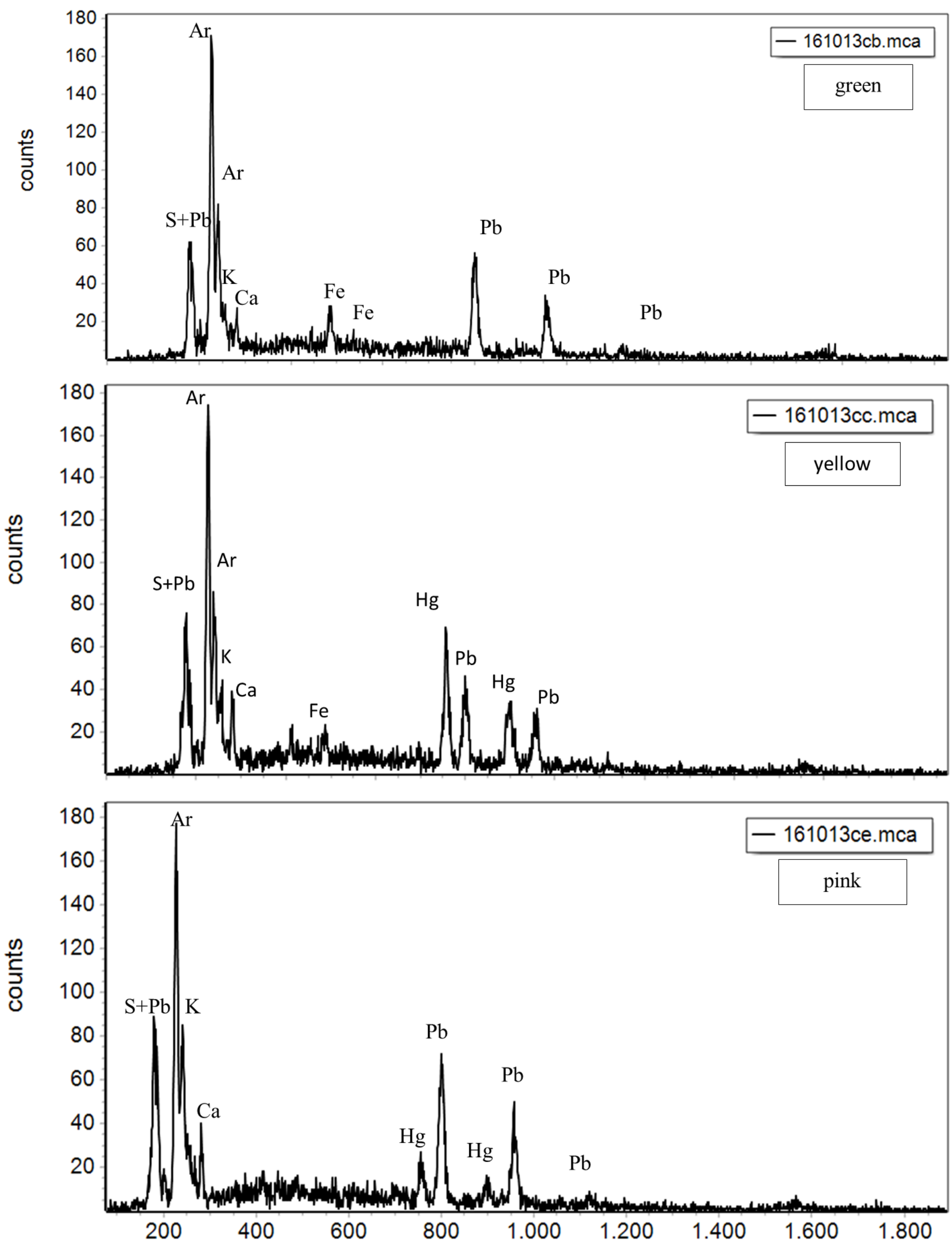


Figure 15 - ED-XRF spectra of item *Inimitable paper* for the green (upper), yellow (central) and pink (lower) pigmentation areas (IFUSP, Ag tube).

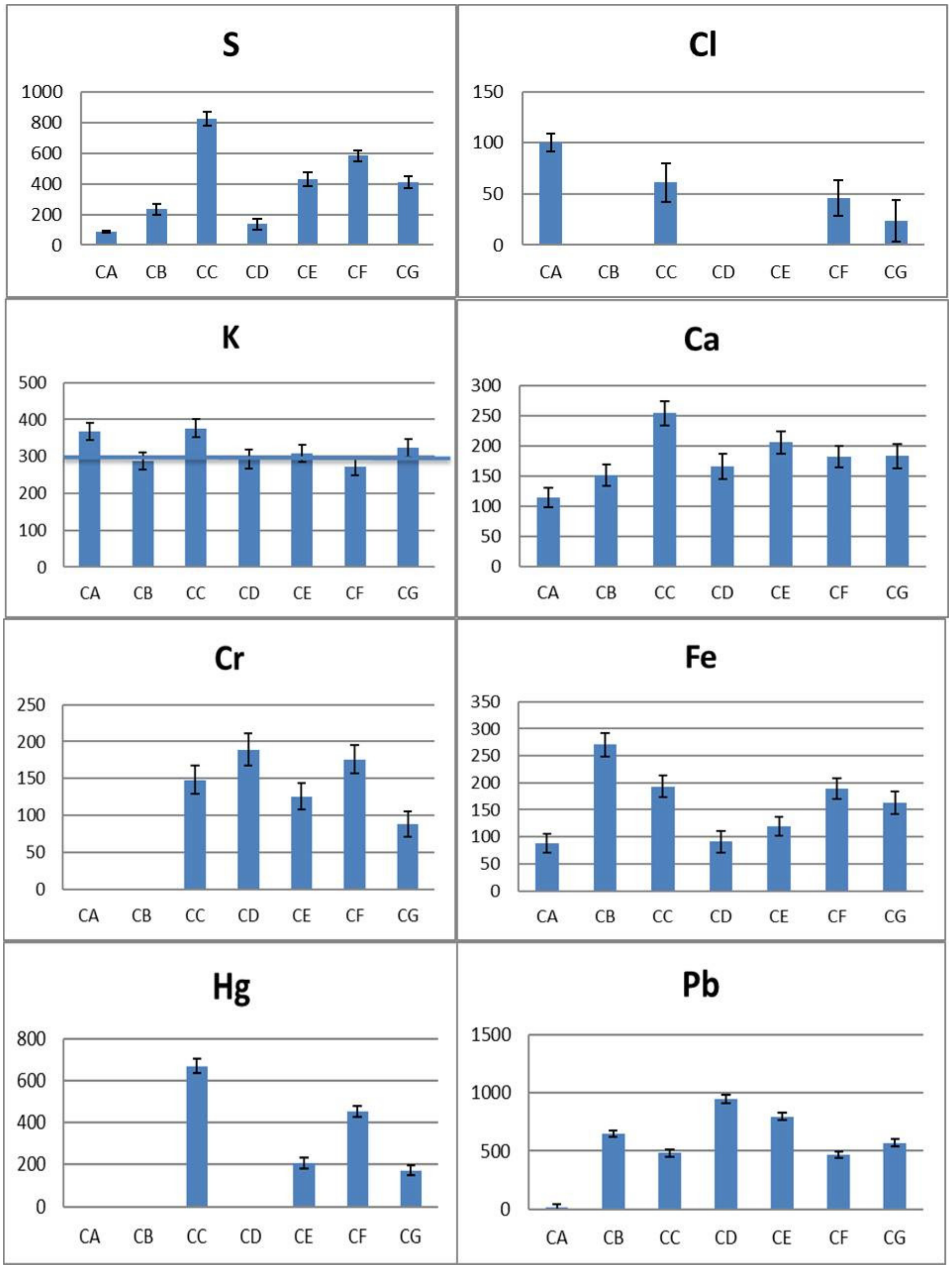


Figure. 16 - Bar charts for each element obtained with the ED-XRF results for item *Inimitable paper* measured at the various points (IFUSP, Ag tube).

The bar charts show that there is a mixture of these chemical elements in the different colors measured. Mercury (Hg) is present in pink and yellow pigments - in higher amounts in yellow points (*cc* and *cf*) - and is not present in the green pigment (*cb* and *cd*) or in the paper (*ca*).

Lead (Pb) was mixed with all inks, at all points measured for the pigments and, to a lesser extent, on the "blank" paper point (*ca*). Potassium (K) is evenly distributed at all points, indicating that it may be related to paper, not to pigments. Iron (Fe) is present at all measured points. Chromium (Cr) is present at all points except *ca* (paper) and *cb* (green) points.

There was also a correlation between the elements sulfur (S) and mercury (Hg), which are present in higher amounts in the pink colored points (confirming the use of *vermilion* or *cinnabar* red pigment).

The lead (Pb) present in pink colored areas may also indicate the use of red lead. Chromium (Cr) may be related to the chrome green pigment appearing at *cd*.

Suggested pigments used by Hercule Florence to make this copy of inimitable paper: white lead, lead-tin-yellow, red mercury, red lead, and chrome green.[28]

XRF analysis indicates some layer and element overlap - a finding compatible with the image manufacturing process, in which pigments were mixed with a sharp object.

The presence of certain chemical elements in Hercule Florence's works may not be intentional, but derive instead from the intersection of techniques (painting, engraving and photography), supports (glass, gum arabic, potash, paper of various kinds), mediums (graphite, India ink, charcoal, watercolors, oil paints, dry pigments) and instruments (brush, dry point, brushes) that Hercule Florence used to carry out his projects.

White color was produced with white lead - the same white lead that Hercule Florence applied to the glass that would be used as a photographic mask[29] or used to print his polygraphs (either as pure color or for creating lighter shades of other colors).

Lead was also used in some red or yellow pigments. Sulfur and arsenic could be present in yellow pigments. Iron was present in some reds, browns, ocher and other colors that had earth as a component.

Some blue pigments had cobalt. Green colors could contain copper and/or chromium.

Some chemical elements may be considered impurities, but their incidental presence on the items may help to reconstruct the environmental conditions of Hercule Florence's workplace.

28. Cf. Stuart (2008).

29. White lead could be applied to completely obliterate the face of the glass where the mixture of soot and gum arabic had left faults: "Il reste toujours des petits points à jour, mais alors on fait tomber du blanc de plomb sur la planche, en l'écrasant entre le pouce et l'index, et si on sent du sable des petits grains durs, on les jette dehors; ensuite on frotte le blanc avec l'index pour l'étendre bien, cela sert à boucher les trous et à blanchir la planche, afin de voir mieux les traits du dessin (...)." (*L'Ami des Arts*, p. 44). It was also used to transfer the contours of the design to the matrix: "On trace d'abord le dessin sur du papier transparent, et on frotte du blanc de plomb sur le dessin, onle fixe sur la planche, et on passe sur le revers un poinçon sur les traits, le dessin se trouve tracé sur la planche en sens opposé, afin que sur les épreuves il soit dans son vrai sens" (*L'Ami des Arts,* p. 45).

30. We thank Professors Carlos Jared, Marta Maria Antoniazzi and Luciana Almeida, from the Butantan Institute's Cellular Biology Laboratory (São Paulo), for the use of the stereomicroscope. The device allows a 20.5:1 zoom to achieve the optical resolution of 0.952 µm.

The presence of cobalt in *Pharmacy Labels* motivated its microscopic analysis. What would be its origin, since its content does not seem to be related to photosensitization?

In an attempt to obtain more information, but still following our option for non-destructive techniques, the Leica M205 A stereomicroscope of the Instituto Butantan (São Paulo) was used.[30] Besides not requiring the removal of a sample, the equipment allows a large zoom (20.5:1 scale) and a three-dimensional reconstitution of the original object by combining a sequence of two-dimensional images.

The tests were reduced to the minimum required to avoid the exposure of the originals to light as much as possible: only one detail of the *Pharmacy Labels* and one of the *Masonic Diploma* were analyzed.

The first analysis showed the well-marked lines of the *Pharmacy Labels* (Figure 17).

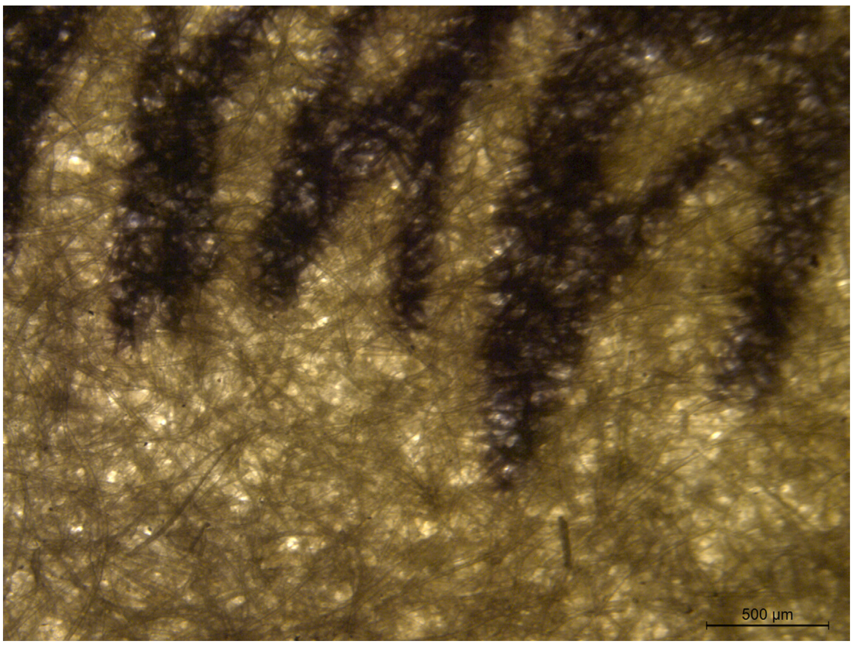


Figure 17 - Image resulting from the analysis of item *Pharmacy labels* obtained with a Leica M205 A stereomicroscope (detail of area with photo printed image). Hercule Florence. [*Pharmacy labels*], [1833-1839]. Photographic copy of pharmacy labels, obtained on photosensitive paper by contact under sunlight, 21.0 x 29.4 cm (irregular). Instituto Hercule Florence Collection (São Paulo). Photo: © Studio 17 - Patricia de Filippi and Millard Schisler

Observation of the *Masonic Diploma* has revealed a possibility deserving further investigation.

The stereomicroscope offers options for object illumination (top, bottom, side). Using this feature we could visualize small particles amid the fibers of the paper in the *Masonic Diploma*. With transmittance illumination (where light "passes through" the work) with the light source placed below the object, these particles appeared dark. With reflectance reading (where the source is above the object and the light is reflected on the analyzed surface), the particles appeared slightly yellow.

Under closer scrutiny (as far as the stereomicroscope lens allowed), the "stains" resemble small fragments of bright material amid the paper fibers.

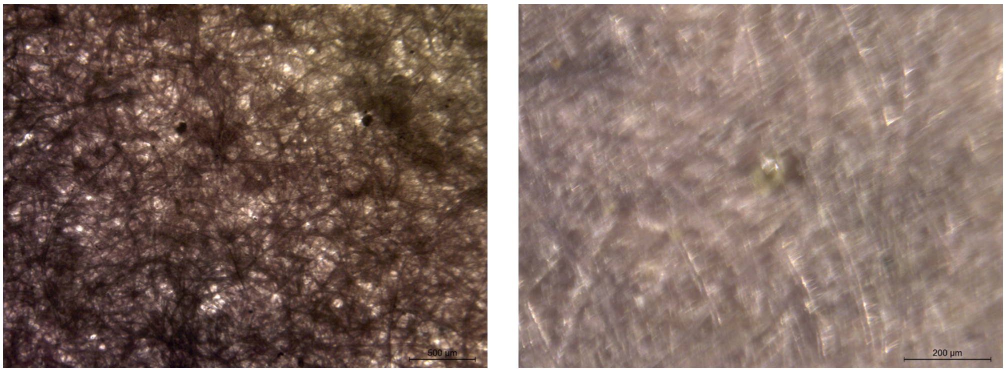


Figure 18 - Stereomicroscopy of *Masonic diploma*. On the left, transmittance illumination shows a dark point; On the right, the light source reflected on the same area causes the particle to appear yellowish. Hercule Florence. [*Masonic diploma*, front and back], [1833-1839]. Photographic copy on photosensitive paper, obtained by contact under sunlight, 20.2 x 29.1 cm (irregular). Instituto Hercule Florence Collection (São Paulo). Photos: © Studio 17 - Patricia Filippi and Millard Schisler

The results of the XRF analysis and Hercule Florence's own handwritten annotations suggest that such fragments are actually macerated gold particles that eventually overlay or incorporate into the paper fabric.

One of the methods tried by the artist was the use of gold chloride. The small solid particles of this metal present in the solution in which the paper was dipped to become photosensitive could explain the results of microscopy analysis.

Further research using optical instruments could include comparative examinations of other prints produced by Hercule Florence, both through polygraphy and *impression à la lumière solaire*. Tests with other methodologies are also being considered, always guided by the principle of preserving the integrity of the originals.

The initial question about the presence of cobalt, however, remains unanswered. A study of the composition of papers available in São Paulo and Rio de Janeiro during the 1830s could also help clarify such questions.

HERCULE FLORENCE, FRIEND OF THE ARTS

The results of the analyses corroborate the notes made by Hercule Florence between 1833 and 1837. In the manuscript *L'Ami des Arts*, Hercule Florence recorded the process of printing by sunlight (which he called *Photograhie*) and fixing images in the *camera obscura*.

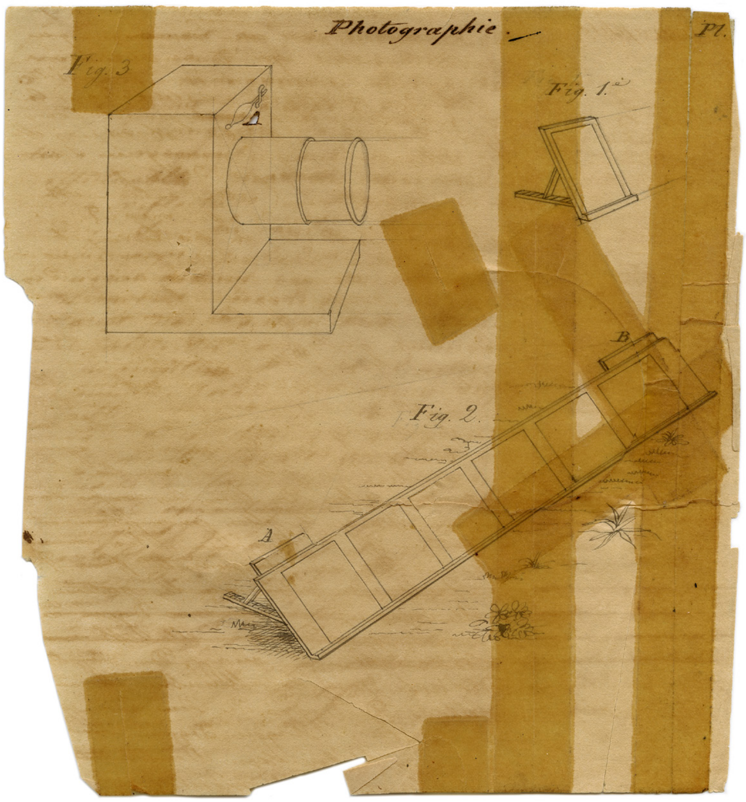


Figure 19 - Hercule Florence. *Photographie*, undated. Iron gall ink on paper, 20.6 x 19.1 cm (irregular). Originally inserted on page 56 of the manuscript *L'Ami des Arts*... Instituto Hercule Florence Collection (São Paulo). Photo: © Studio 17 - Patricia de Filippi and Millard Schisler

Especially in 1833 and 1834 some experiments are mentioned involving silver nitrate,[31] gold chloride[32] and flowers of sulfur[33] as photosensitive reagents.

After 1834, Hercule Florence continued his research and experiments, but the notebooks recorded only his reading notes[34] - especially on the reduction[35] or dissolution[36] of gold, reactions that would help him create his photographie dorée.[37]

In 1837 and 1838 he wrote: "Silver nitrate and chloride,[38] and gold chloride are the only reagents with which I did my experiments because I had no others at my disposal."[39]

He added that gold chloride "should serve as printing ink; it is extremely expensive, but its properties are such that I am obliged to prefer it to silver nitrate or chloride, which is four or six times cheaper."[40] And he insisted: the biggest disadvantage of his invention was the high price of the ink, because "it is gold itself."[41]

Silver nitrate,[42] a compound with which he "printed for a long time," also produced good results. However, when the paper was of high quality, the notes mention gold chloride. At the end of his memories, Hercule Florence mentions one of the qualities of this substance, which was to react very well to the fixative (urine): "it immediately becomes a beautiful bluish black."[43]

The physicochemical analyses carried out at IFUSP, IPEN and Instituto Butantan in 2016 allowed us to combine the author's texts and practical results for the first time, but many gaps still need to be filled.

It is possible to deduce that Hercule Florence's empirical experiments (with both gold chloride and silver nitrate) were far more numerous than the surviving items or records in his manuscripts indicate.

In the *Livre d'annotations*, written between 1829 and 1834, Hercule Florence repeatedly cites labels, especially the pharmacy labels, as examples of the practical application of his invention and of the relationship between different printing techniques[44] (referring to photography and polygraphy).[45] There are no descriptions, however, of actual tests. We may surmise, then, that the pharmacy labels that have survived to our day were made as experimental procedures aimed at future elaborations and commercial uses.

References to the Masonic diplomas are even scarcer: there is no explicit mention. There are, however, some notes related to Freemasonry.[46] In any case, it seems quite logical that the Masonic diplomas produced using *photographie* would be considered objects of prestige.

All of these elements make it possible to date with great certainty the photographic experiments with gold salts from April 1833. It is difficult, however,

31. $AgNO_3$. *Livre d'annotations...*, p. 131v-133v (January 20, 1833); p. 136v (February 14, 1833); p. 137bis (March 9, 1833); 139bisv (March 12, 1833); p. 14 bis (April 4, 1833); p. 144bis (April 27, 1833); p. 144bisv (June 7, 1833); p. 147v (July 1, 1833); p. 157v-158v (February 15, 1834; an experiment that would have allowed him to obtain a lightening rather than a darkening; *L'ami des arts...*, p. 61).

32. $AuCl_3$. *Livre d'annotations...*, p. 141bis-142bisv (April 8, 1833); p. 143bis (April 20, 1833).

33. *Livre d'annotations...*, p. 144bis (April 26, 1833). From this date, there are no further mentions of the flowers of sulfur.

34. For the products mentioned by Hercule Florence, cf. *Livre d'annotations...*, p. 135, 136v, 139bisv, 143bis-144bis, 145bis-146, 148v-150, 153-153v, 155-157, 164v-166; *2e livre...*, p. 17-21, 38-42, 44-53, 55, 67. See also *L'ami des arts...* (p. 53 and especially p. 57-58). His notes are reworked on p. 63-77. Florence also considered using electricity - initially to deoxidize "une dissolution of nitrate d'argent" (*2e livre...*, p. 34-35), and later for direct printing (p. 101-102).

35. *Livre d'annotations...*, p. 161-161v (April 1834).

36. *2e livre...*, p. 49 and 53 (both undated, probably 1837).

37. Term used twice: *2e livre...*, p. 37 (April 19, 1837) and p. 50 (probably 1837).

38. Silver chloride: AgCl.

39. "Le nitrate et le chlorure argentiques, et le chlorure aurique sont les seuls corps sur lesquels j'ai fait mes

to extend them beyond May 1839, when Hercule Florence became aware of the "discovery of Daguerre."

Simultaneously with his researches on photography, Hercule Florence investigated polygraphy - conceived two years earlier, less expensive, less demanding (photography required sunny days).

Throughout the 1830s, Hercule Florence found himself hesitating between these two different techniques, but which addressed similar questions. The artist-inventor wanted to find a way to print easily, with reduced costs and means. Polygraphy dispensed with lithographic stones and the heavy press. Photography seemed to go further, reducing the effort and materials required, allowing some materials to be carried easily, but at a higher price and more unstable result. The manuscripts follow the inventor's doubts and hesitations.[47]

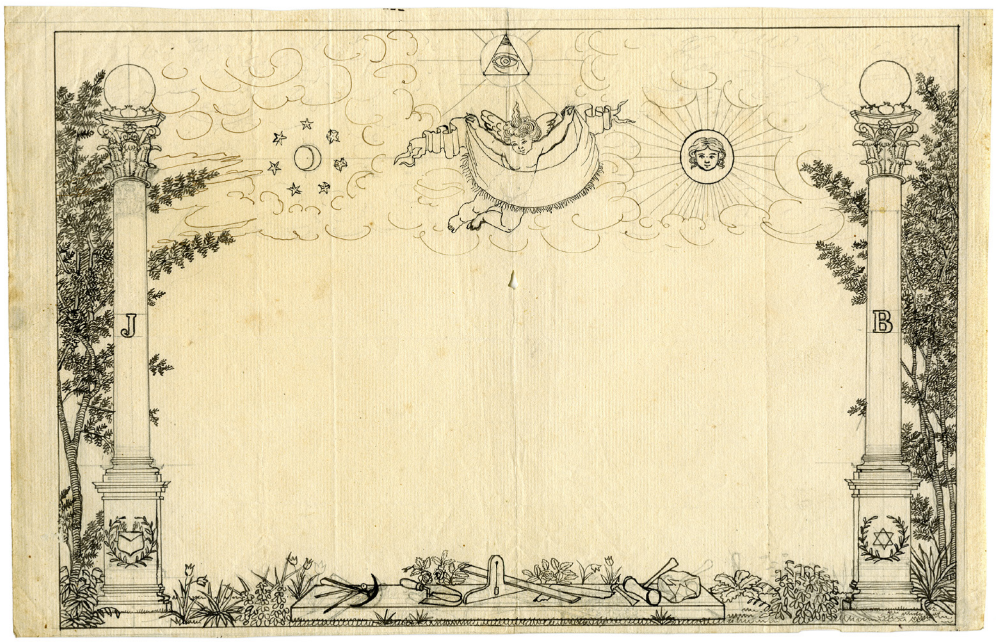


Figure 20 - Hercule Florence. [*Masonic diploma*], [1833-1839]. India ink and graphite on paper, 19.2 x 30.2 cm (irregular). Instituto Hercule Florence Collection (São Paulo). Photo: © Studio 17 - Patricia de Filippi and Millard Schisler

expériences, parce que je n'en avais pas d'autres", in L'ami des arts, p. 74. Yet he admits unsuccessfully trying some mercury salts (p. 75). In *Livre d'annotations...* et le *2e livre...* Hercule Florence mentions many other elements and compounds that would probably change color in light, but which he could not test for lack of resources.

40. *L'ami des arts...*, p. 46. It is important to remember that the chemical elements nitrogen (N) and silver (Ag) were not found in the tests.

41. *L'ami des arts...*, p. 3.

42. *L'ami des arts...*, p. 42. See also *L'ami des arts...*, p. 50-51. We have indirect clues about experiments with silver chloride in L'ami des art ...; on the margin of p. 57, an interesting note: "some of the rays of the solar spectrum communicate their color to silver chloride!" See also p. 61-62, 68. Hercule Florence broadly describes an earlier untraceable experiment. P. 73 contains a record of an unsuccessful experiment.

43. *L'ami des arts...*, p. 74.

44. *Livre d'annotations...*, p. 148 (July 6, 1833); p. 150v-151 (August 26, 1833). See also *L'ami des arts...*, p. 54

45. *Livre d'annotations...*, p. 158v, where polygraphy is still called Papier autographe (February 15, 1834).

46. P. 153v-154v. See also *Livre d'annotations...*, between October 20 and 27, 1833. The relationship between Hercule Florence and Freemasonry is still to be deepened. At least once he refers to ideas related to Freemasonry in *Livre d'annotations* (October 20 and 27, 1833).

47. For comparisons made by Hercule Florence

The Hercule Florence Institute keeps a preparatory drawing for the Masonic diploma, executed in India ink and graphite. There are slight differences in both content and proportions between this drawing (Figure 20) and the corresponding *photographie*, as Hercule Florence called it (Figure 3).

The process used by Hercule Florence to reproduce the drawing using sunlight is still unclear. It is likely that the India ink drawing was the first step in the process that would result in the *impression à la lumière solaire*.

This process would also involve a "transfer" to a "transparent paper" (with the back covered by white lead and which, due to its fragility and wear, would not have resisted) and a glass slide in which the contours of the drawing would be "printed" on the face covered with a mixture of soot and gum arabic.

Once the matrix with grooves for light to pass through was ready, the glass would then be exposed to the sun. The differences between the drawing and the printed image of the *Masonic Diploma* could be due to the thickness of the glass, which would be positioned at a small distance from the photosensitive paper.

The scientific analyses described in this paper allow us to formulate some hypotheses.

The presence of the element gold Au (and not silver Ag) in the *impressions à la lumière solaire* (made in the early 1830s) suggests that Hercule Florence was a world pioneer in the use of gold salts in the sunlight-printing process. This argument is also based on the remarkably sharpness of the *Pharmacy Labels*, while the absence of detectable gold in the *Masonic Diploma* may explain its fading.

The other chemical elements found in the three samples provide information about the procedures and materials used in his researches. The element lead (Pb), found in the two *épreuves photographiques* in both larger and smaller amounts, can help to clarify how the photographic matrix was prepared, which included the application of white lead pigment on the back of the "transfer."

In any case, we hope this article will allow other scholars, now aware of the steps of Hercule Florence, to unravel more details about his photographic process.

His experiments with *photographie* and polygraphy techniques were guided by practicality, economy and efficiency, characteristics that were dear to him. Hercule Florence, self-styled *Ami des arts*, was a humanist, a true friend of the arts and applied sciences, guided by ideas that were to bring advancements and development not only to his Nineteenth-century contemporaries but also to the following centuries.

between photographie and polygraphie (April 1837), cf. *2e livre*..., p. 40-41. See also the polygraphy of pharmacy labels from the Cyrillo Hercule Florence Collection, reproduced in Florence (2009, p. 128).

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