

**NON-DESTRUCTIVE ANALYSES:
CREATING STANDARDS FOR IMPERIAL
BRAZILIAN STAMPS FROM A CASE STUDY OF
COTTENS ESSAYS**



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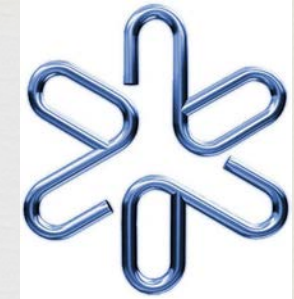
São Paulo Philatelic Society (Sociedade Filatelica Paulista – SPP)

Brazilian Philatelic Federation (Federação Brasileira de Filatelia – FEBRAF)

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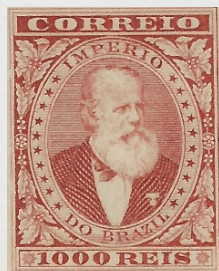
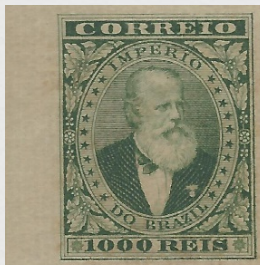
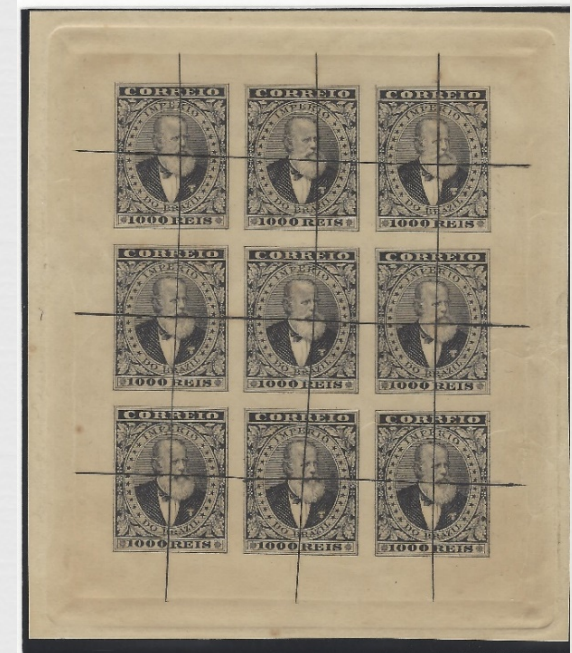
Coordinator of the Nucleus of Physics Research Applied to the Study of Historical
and Artistic Patrimony NAP-FAEPAH.

What are Cottens Essays?



The Emperor Peter II white-beard Brazilian postal essays.

The stamps might have been issued had the Empire continued and the Republic not been proclaimed in 1889.



Looking for the History



❧ Why?

❧ The historical research.

❧ Name "Cottens".

❧ The photo.



❧ The difficulties.

❧ Youtube: "Filatelia | Ensaio de Cottens".

❧ Analytical Methods on Philately.

State of the Art



- ❧ Progress in the analysis of historical patrimony.
- ❧ University of Sao Paulo – USP.
- ❧ Just one paper about Brazilian philately (2016):
 - ❧ Schwab et al. 2016. Energy Dispersive X-Ray Fluorescence Profile of Some Brazilian Postage Stamps. *Journal of the Brazilian Chemical Society*.
- ❧ International papers published on analytical methods in philately.
- ❧ A new way:



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Solving Philately's Puzzles through Science™

Purpose



☞ Main purpose:

- ☞ To lay the groundwork for analysis of the Imperial Brazilian postal stamps via a case study of the Cottens Essays, creating standards of analysis.

☞ Secondary purpose:

- ☞ To discover more about the Cottens essays, mainly about their origin: ABN Co., Brazilian Mint or another issuer.

The Printing Contracts (69 stamps)



☞ **Brazilian Mint:**

- ☞ 1843: Bull's Eyes set.
- ☞ 1844: Snake's Eyes set.
- ☞ 1850: Goat's Eyes set.
- ☞ 1854/61: Cat's Eyes set.

☞ **American Bank Note Co.:**

- ☞ 1866: Emperor Peter II Perforated Black Beard set.
- ☞ 1876: Emperor Peter II Rouletted Black Beard set.
- ☞ 1877/78: Emperor Peter II Rouletted White Beard set.

☞ **Continental Bank Note Co.:**

- ☞ 1878: Emperor Peter II "Orange and Green".

☞ **Brazilian Mint:**

- ☞ 1881: Emperor Peter II Small Head set.
- ☞ 1882/85: Emperor Peter II Large Head set.
- ☞ 1883: Emperor Peter II Cross and lined background.
- ☞ 1884: Emperor Peter II Little Head.
- ☞ 1884/88: Types Cipher, Southern Cruise, Imperial Crown and Sugar Loaf Bay set.

Samples



All the stamps were analysed *in natura*, without any special preparation and avoiding, as a rule, the analysis of the gum and the rubber ink stamps.

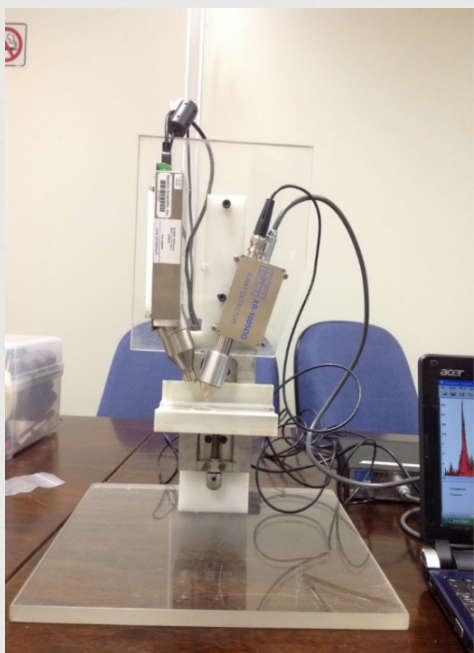


Starting the Analytical Studies



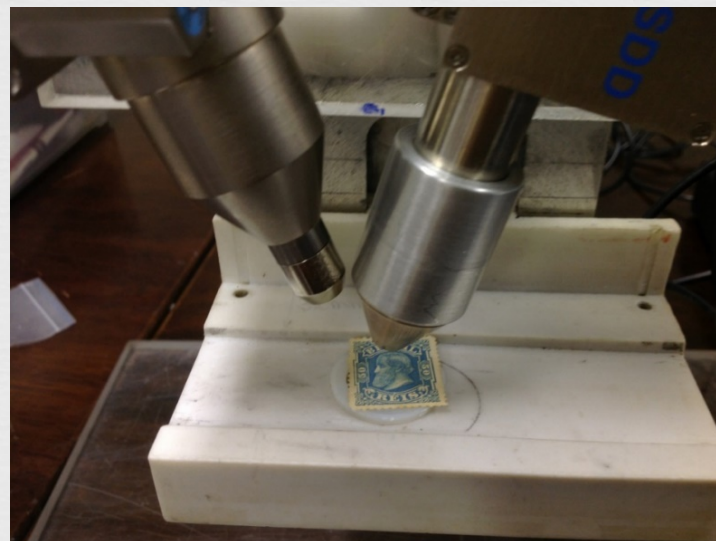
- ❧ X-Ray Fluorescence (XRF).
- ❧ X-Ray Spectroscopy (PIXE).
- ❧ Optical Microscopy.
- ❧ Paper Thickness.

X-Ray Fluorescence (XRF)



The X-Ray Fluorescence Analyzer – XRF – is a non-destructive analysis technique, which has been widely used to investigate the elemental composition present in certain materials, including in postage stamps.

The applied voltage for the x-ray tube was 30 kV and the current accepted was 10 μ A. The samples were irradiated for 200 seconds.

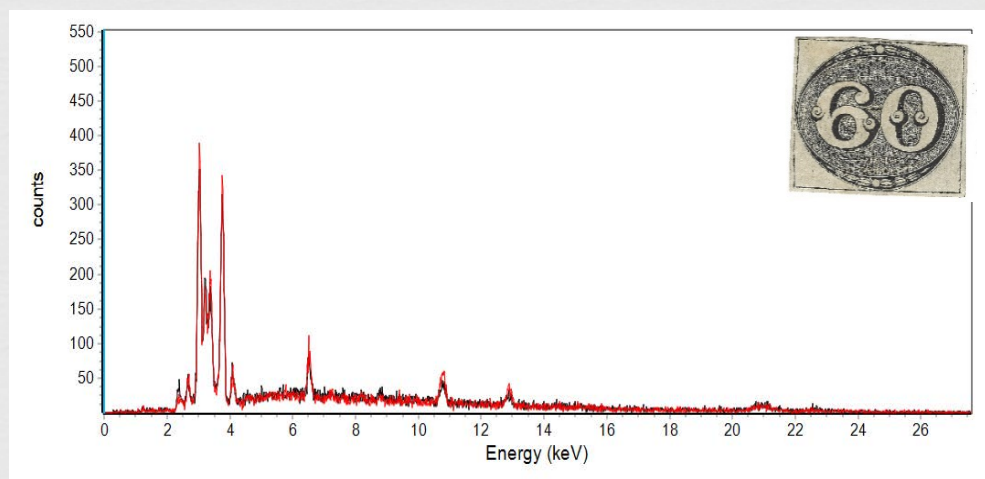


XRF Analysis – Obverse and Verse



❧ The analysis of the obverse and verse of the stamps by means of the XRF technique are the same.

❧ The beam has a depth that affects practically the entire thickness of the stamp.



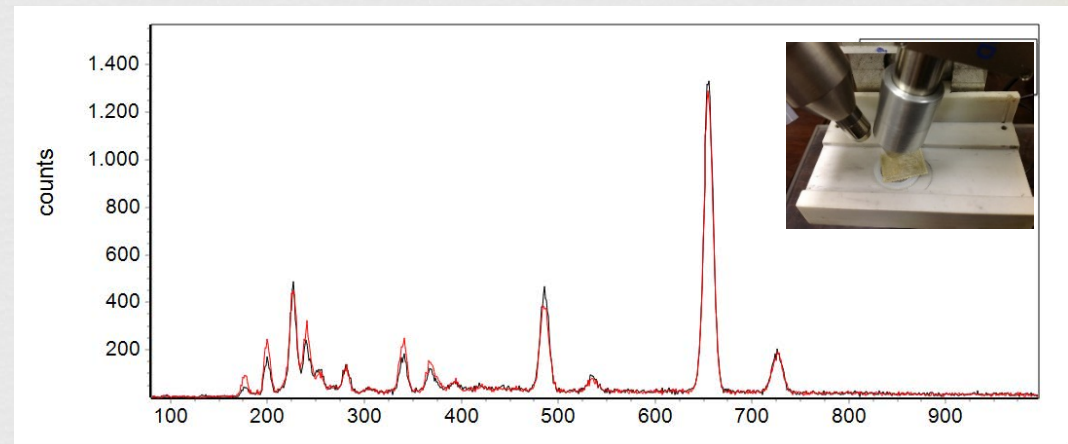
❧ This is an important difference from the results from the PIXE which allows a very superficial analysis.

❧ Not important to paper.

XRF Analysis - Gum



✎ The presence of gum in the stamp present a different result, since there are more chemical elements attached to it on the verse.



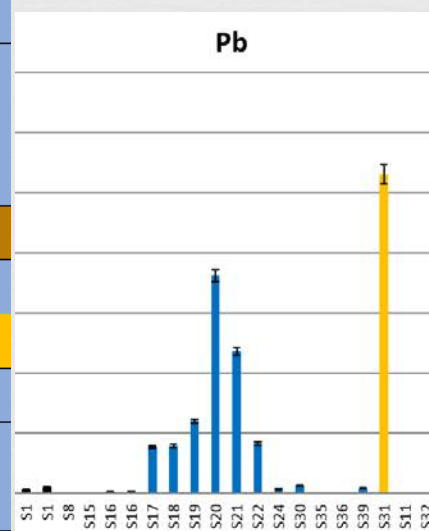
✎ The gum has more barium (Ba), potassium (K), chlorine (Cl) and sulfur (S), while the obverse of the stamp has more iron (Fe) and zinc (Zn), which are elements used in the Prussian blue pigment or lithopone.

XRF Analysis – Brazilian Mint – Lead (Pb)



Issue	Sample	Intensity	Color
1843	S1	41	Black
1850	S8	0	Black
1854	S16	24	Dark blue
1854	S17	107	Greyish blue
1854	S18	122	Greyish blue
1854	S19	180	Dark blue
1854	S20	512	Blue
1854	S21	342	Blue
1854	S22	134	Blue
1854	S24	41	Greyish blue
1881	S15	0	Blue
1884	S32	0	Pale brown
1885	S30	47	Blue
1885	S31	823	Orange
1885	S39	39	Blue
1887	S35	0	Ultramarine
1888	S36	0	Ultramarine

Blue stamps: indicating Pb as a whitener, considering that there is no blue pigment with this element.

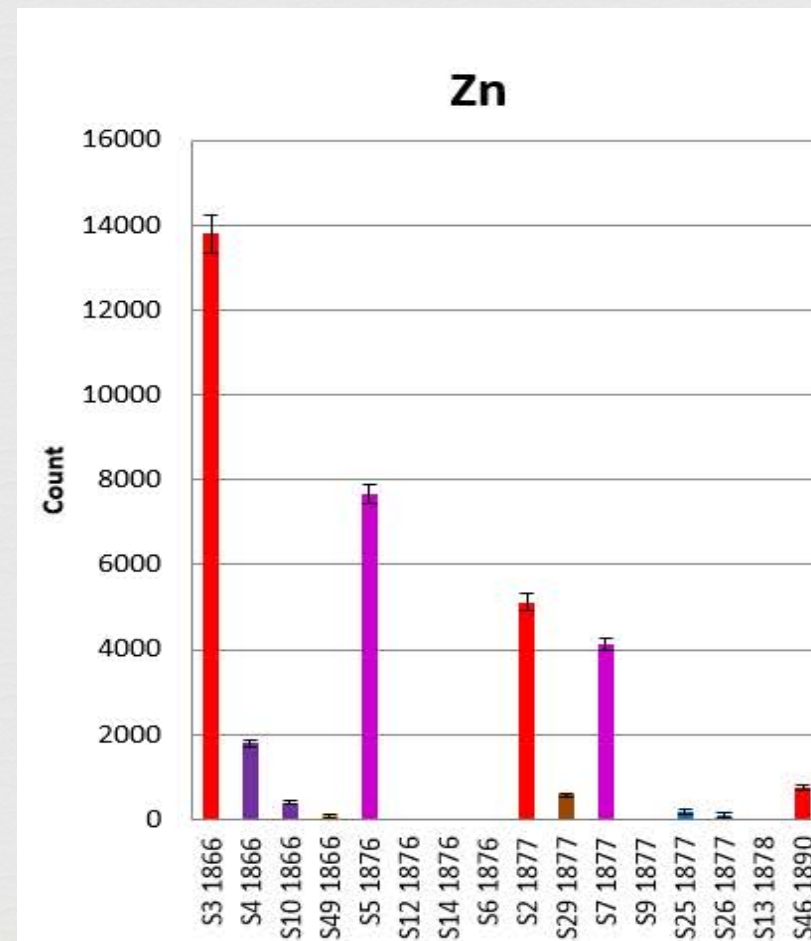


The absence of chromium (Cr) precludes the use of pigments bound to lemon yellow.

XRF Analysis – ABN Co. – Zn and Ba



- ☞ The difference in the emissions of ABN Co. for the presence of zinc (Zn).
- ☞ The only sample in the black color that presented barium (Ba) was the stamp produced by ABN Co.



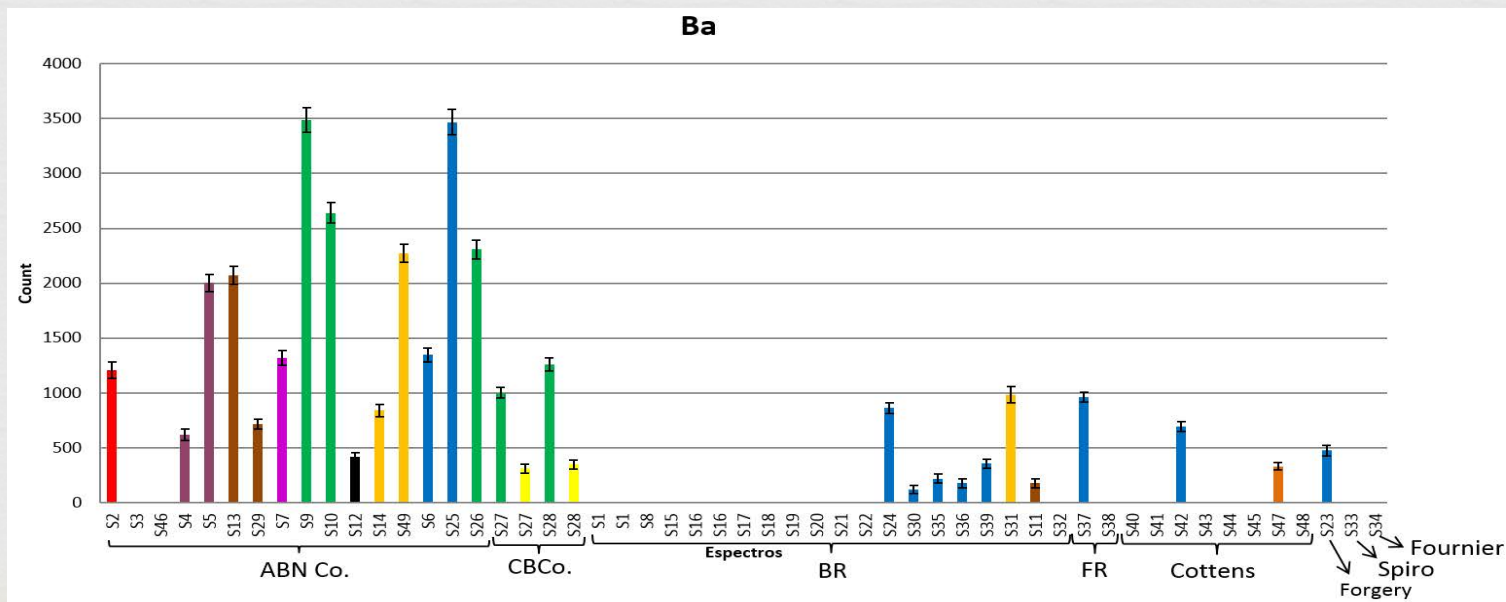
XRF Analysis – Differences of Barium (Ba)



☞ The barium (Ba) is more common in Brazilian stamps produced by the ABN Co. in different colors than in other samples.

☞ Barium (Ba) was used in the whitener pigment in the stamps issued by ABN Co. and mainly after 1881 by the Brazilian Mint.

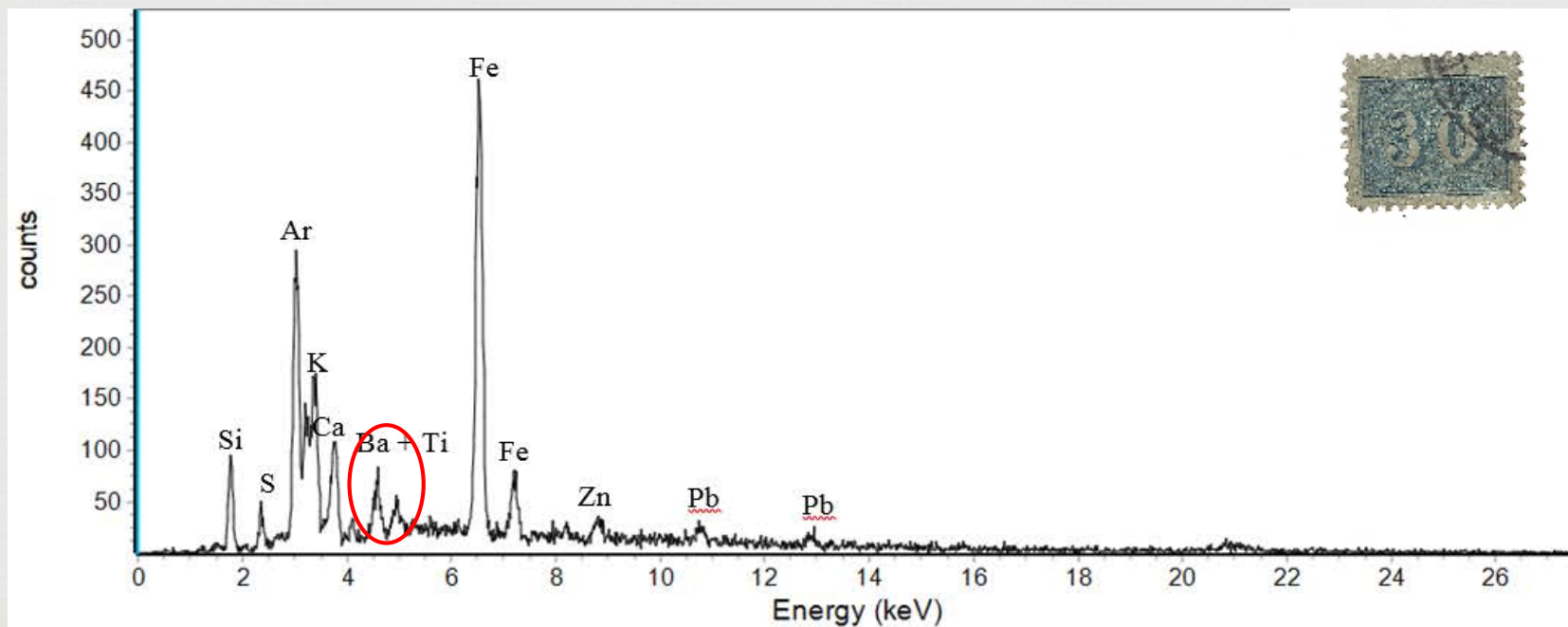
☞ The Brazilian Mint mainly used the lead (Pb) from 1843 to 1861 as whitener pigment.



XRF Analysis – Ba, Ti and Forgery



- ❧ The Cat's Eyes 30 reis Perforated Forgery has barium (Ba), which is not consistent with the issuing period of Cat's Eyes set.
- ❧ In addition, this forgery has titanium (Ti), which is used in pigments post 1920. So, it is a modern forgery.



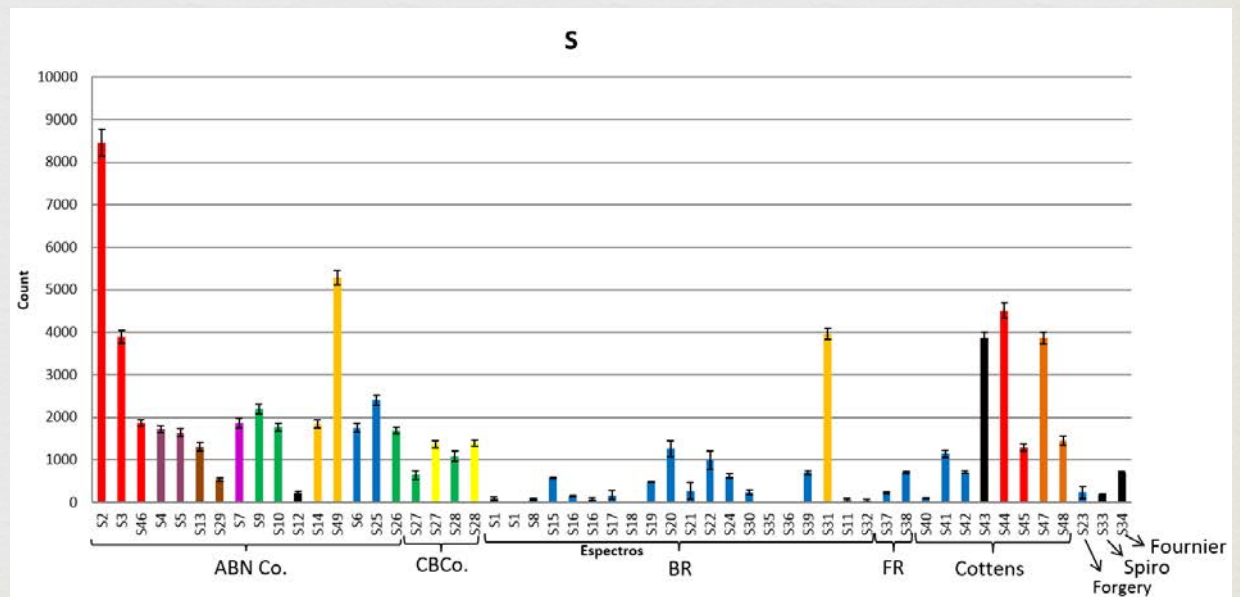
XRF Analysis – Differences of Sulfur (S)



❧ The sulfur (S) level in all Cottens essays differs greatly from the Brazilian Mint pattern, approaching more to the ABN Co. standards.

❧ Incidentally, by analyzing the histograms of all the samples, a different pattern is found for the Cottens essays, indicating that the essays were not issued by the printers in the analysed period.

❧ Sulfur (S) in two red and one orange essays indicates the use of vermilion (HgS) that does not exist in the orange essay with thin paper, which is based on lead (Pb).

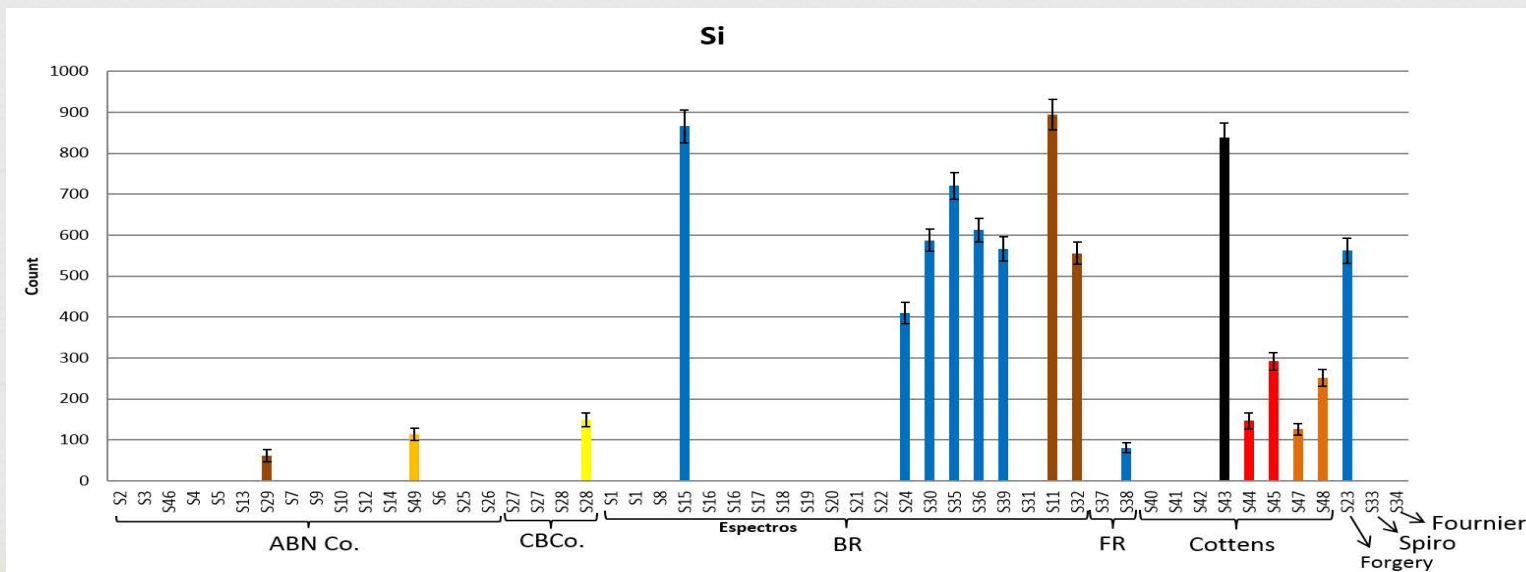


XRF Analysis – Differences of Silicon



❧ The silicon (Si) is present in higher intensity in Brazilian stamps and to a lesser extent in the Cottens essays.

❧ The Brazilian Mint began to use silicon (Si) more in the 1880s and linked to the blue stamps, during which it also used aluminum (Al).



Partial Conclusions about the Ink

S	Color	Probability of Inks	
		Color based on	White based on
S1	Black	Iron oxide / Lead oxide	Calcium sulfate / Calcium carbonate
S8	Black	Iron oxide / Bone black (C+Ca ₃ (PO ₄) ₂) (?)	calcium phosphate (Ca ₃ (PO ₄) ₂) (?)
S16	Dark blue	ferric tannate	Calcium sulfate
S17	Greyish blue	ferric tannate	White lead / Calcium-based
S18	Greyish blue	Prussian blue	White lead / Calcium-based
S19	Dark blue	Prussian blue / ferric tannate (?)	White lead / Calcium-based
S20	Blue	ferric tannate	White lead / Calcium-based
S21	Blue	ferric tannate	White lead / Calcium-based
S22	Blue	ferric tannate	White lead / Calcium-based
S24	Greyish blue	ferric tannate	Lithopone
S15	Blue	Prussian blue	Calcium sulfate / Calcium carbonate / Kaolin, Aluminum silicate (Al ₂ O ₃ 2SiO ₂ .2H ₂ O), and Gypsum, Hydrated calcium sulfate (CaSO ₄ .2H ₂ O)
S32	Pale brown	Organic pigment	Kaolin, Aluminum silicate (Al ₂ O ₃ 2SiO ₂ .2H ₂ O), and Gypsum, Hydrated calcium sulfate (CaSO ₄ .2H ₂ O)
S30	Blue	Prussian blue + Ultramarine	Calcium carbonate / Barium carbonate / Lead white (PbSO ₄)
S31	Orange	Lead oxide, as lead red (Pb ₃ O ₄)	Lithopone
S39	Blue	Prussian blue + Ultramarine	Calcium carbonate / Barium carbonate / Lead white (PbSO ₄)
S35	Ultramarine	Prussian blue	Calcium carbonate / Barium based.
S36	Ultramarine	Prussian blue	Calcium carbonate / Barium based.

Vermilion

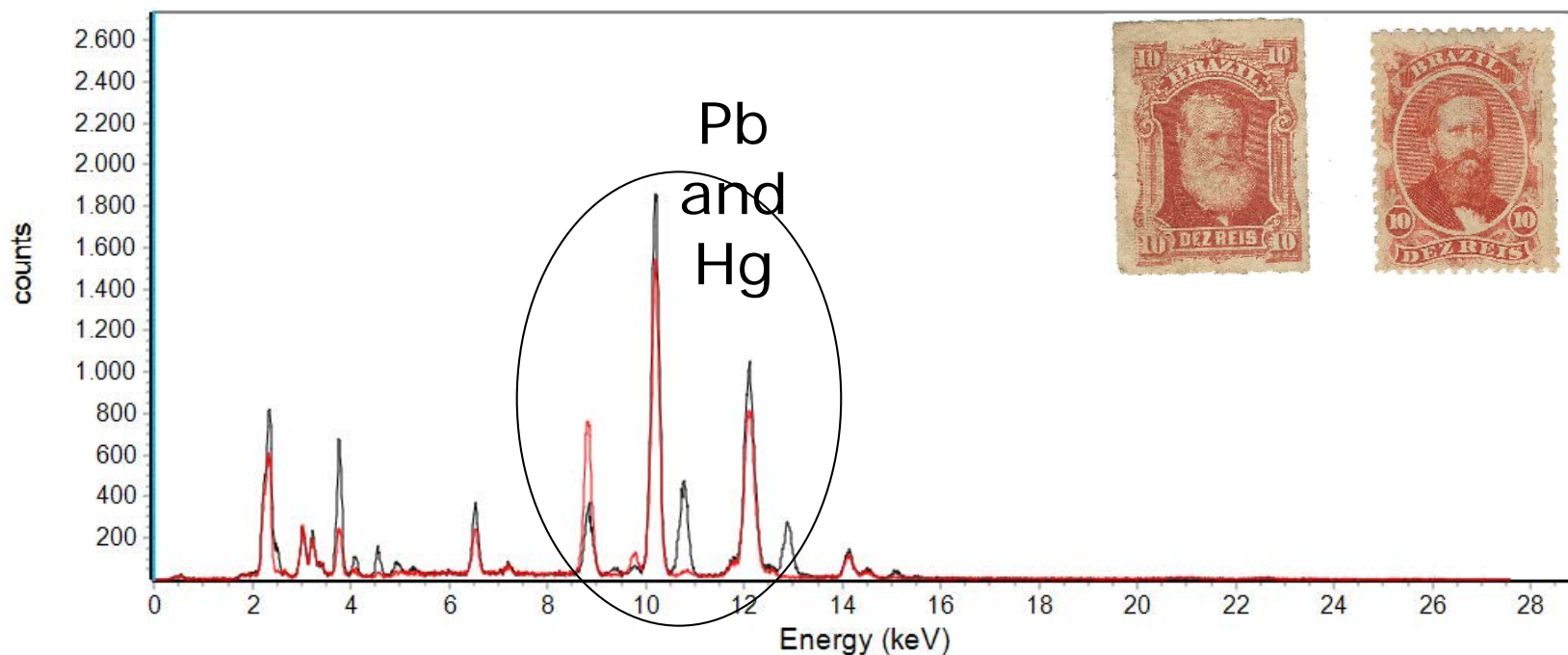


- ❧ The red and orange Brazilian stamps do not use the vermilion for the period from 1881 to 1888.
- ❧ This generates a divergence with the production of the Cottens essays, which used vermilion for the red and orange pigment.
- ❧ Only the orange essay in thin paper did not present mercury (Hg) in its composition, but rather lead (Pb).
- ❧ In this essay, the chromium (Cr) is present in high quantities, which is not a usual element, much less for Brazilian stamps.

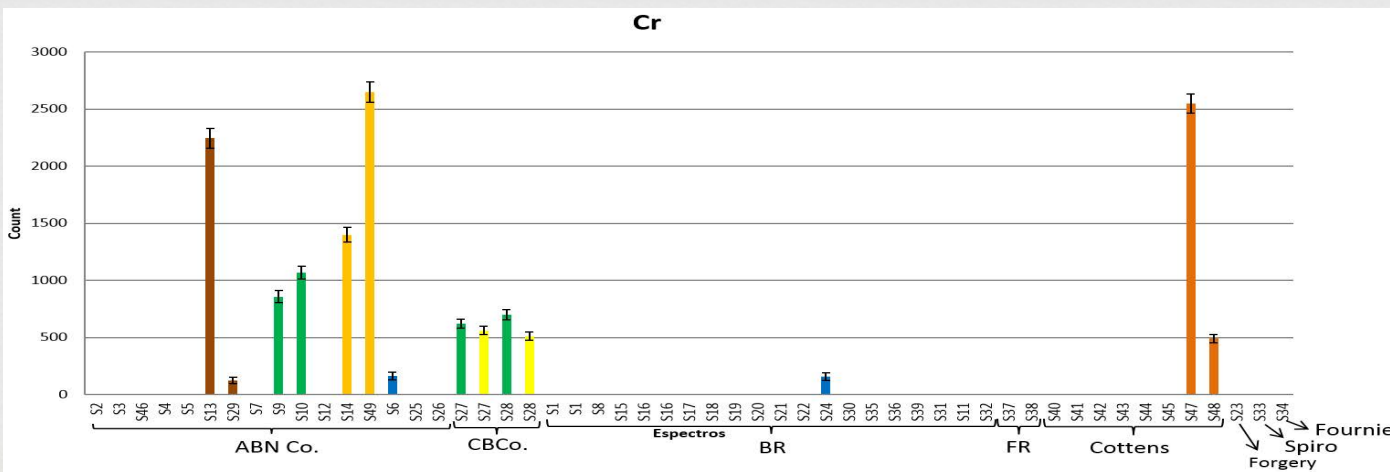
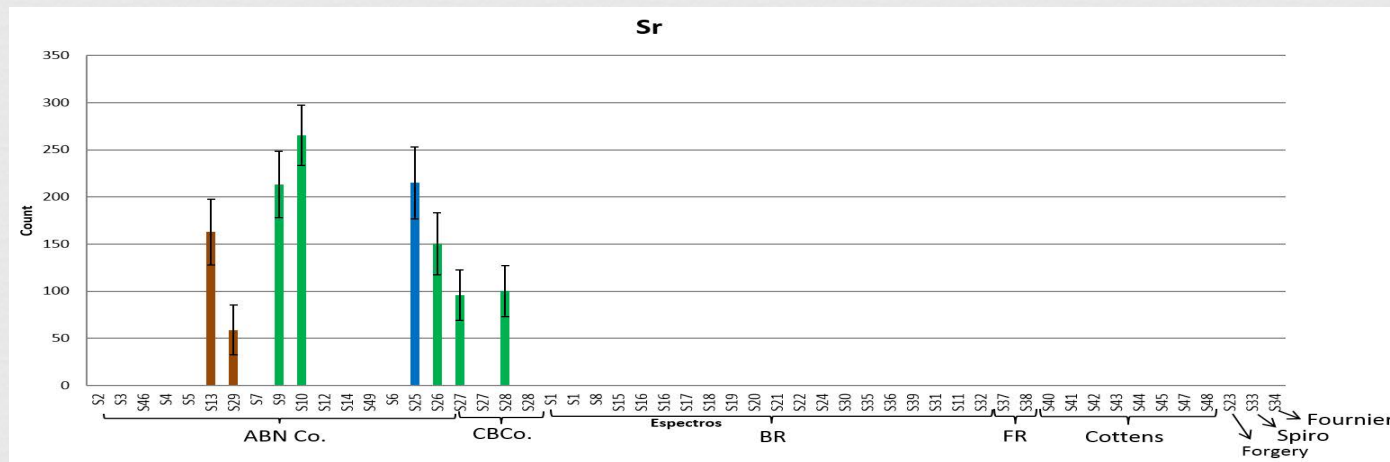
Vermilion and the ABN Co.



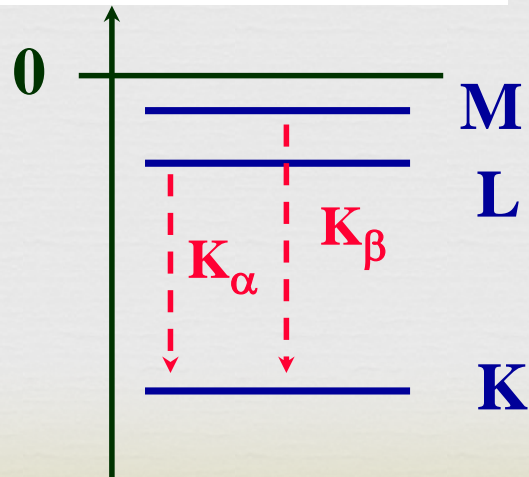
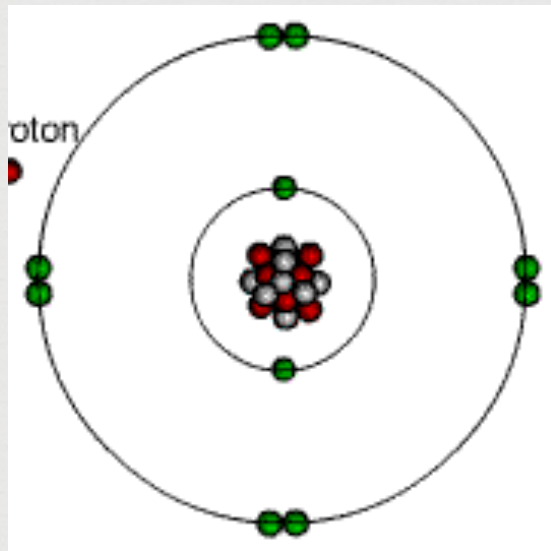
- ❧ The spectra of the red stamps (1866 and 1876) measurements show a high amount of mercury (Hg) and lead (Pb), suggesting the use of the vermilion pigments (HgS) and lead white (PbSO_4).



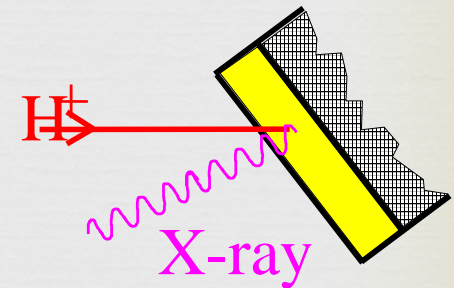
Other elements



X-Ray Spectroscopy (PIXE)



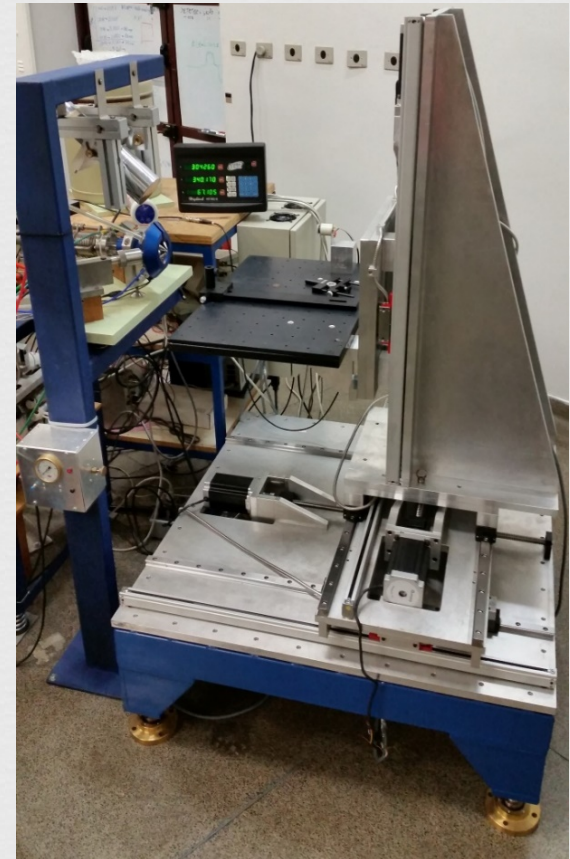
- Non-destructive.
- Highly sensitive physical method of multi-element quantitative analysis.
- Superficial:
 - 25,5 microns in bronze.
 - 100 microns in cellulose.
- 10-20 min.
- Identify and quantify elements with $Z > 10$
- High resolution for nearby elements.
- Low error ~ 5%



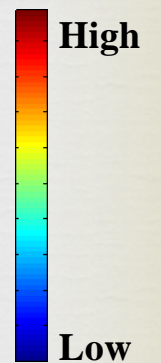
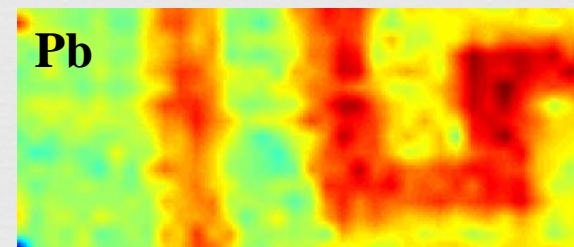
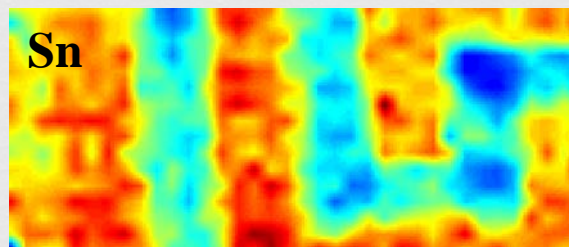
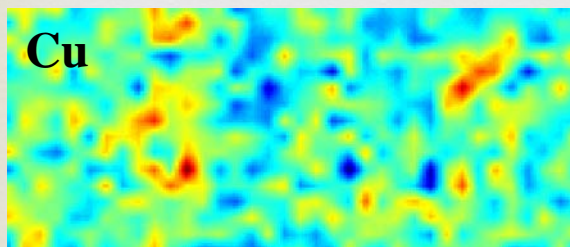
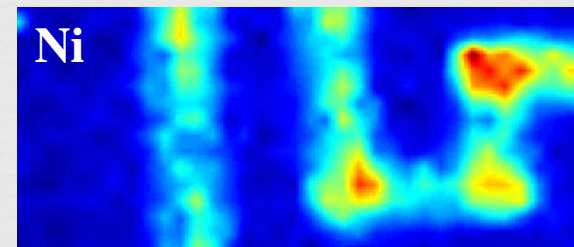
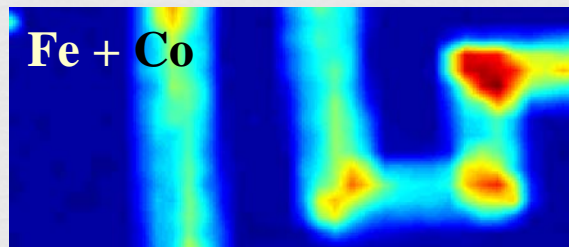
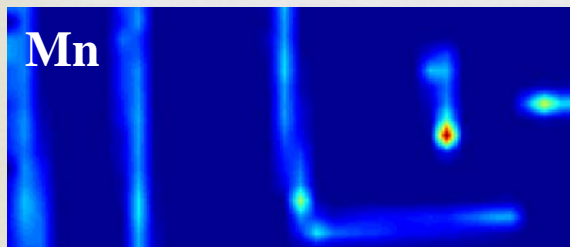
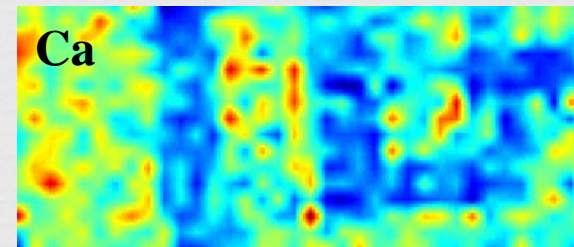
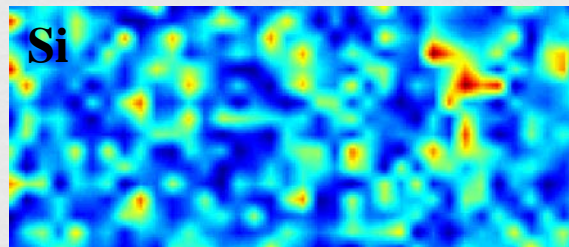
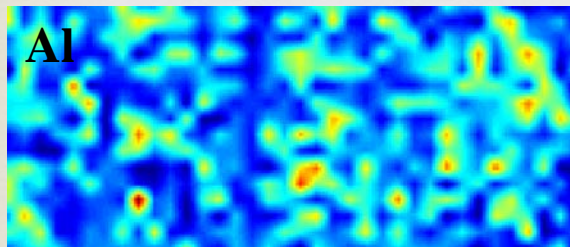
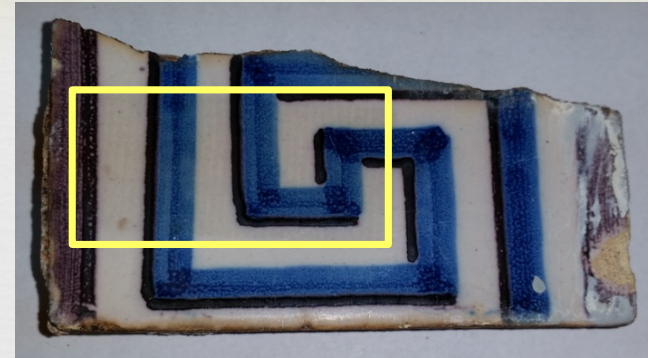
PIXE – Particle Accelerator



PIXE



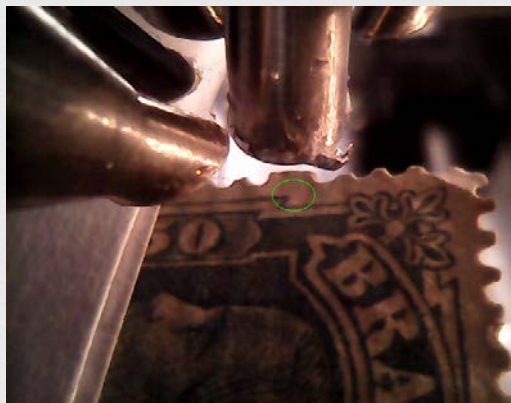
PIXE Results mobile platform (ceramic tile)



PIXE Analysis



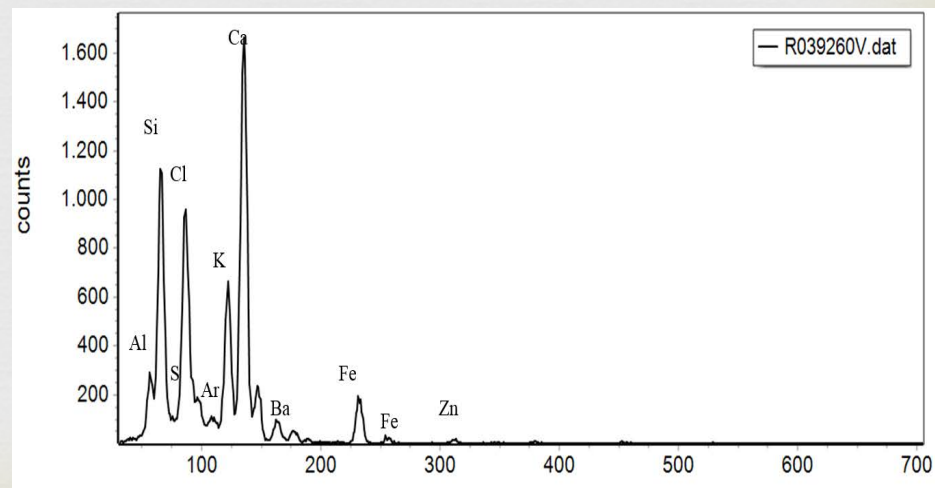
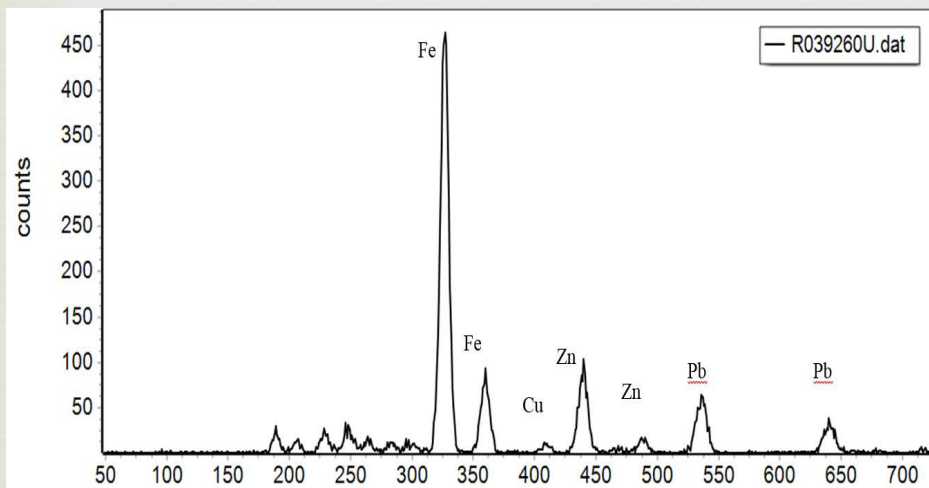
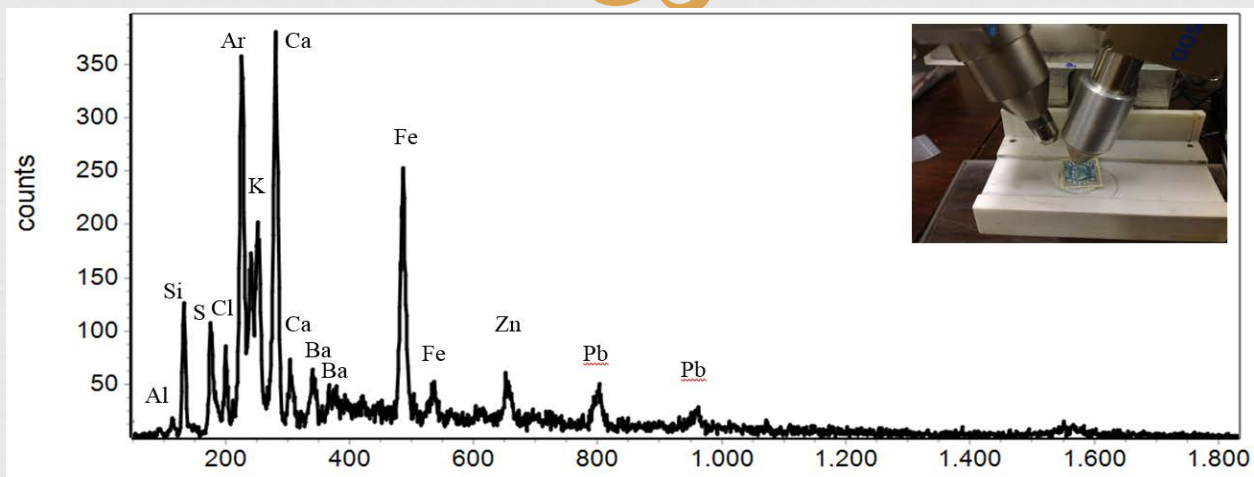
☞ The results of the PIXE analysis of the Emperor Peter II Large Head 50 reis blue stamp corroborated the data collected by the XRF for the same sample.



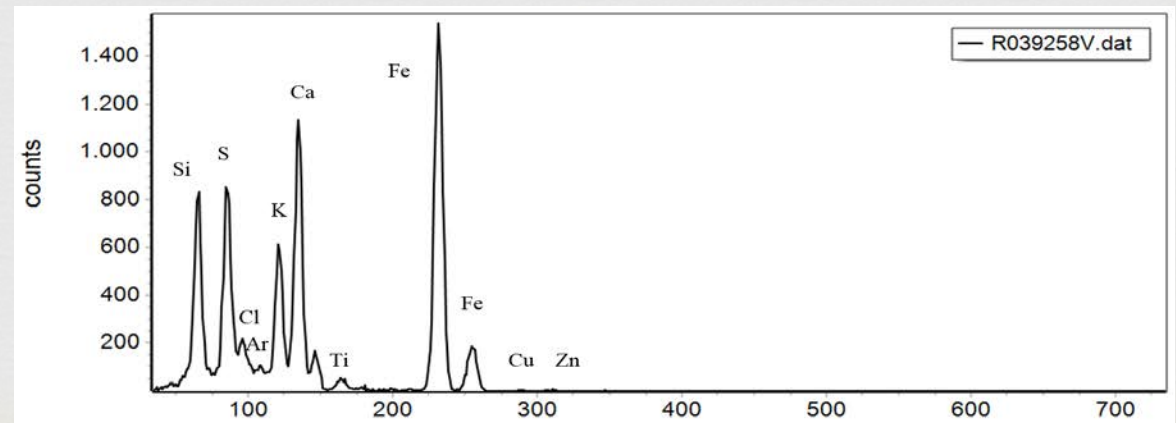
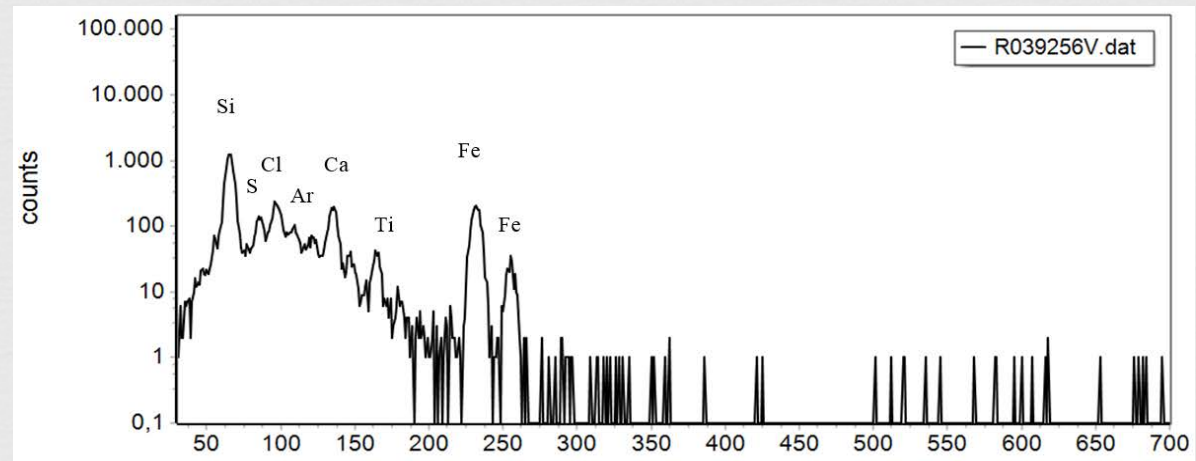
☞ The main difference between XRF and PIXE analyses is the depth of the rays in the sample.



XRF x PIXE



PIXE Analysis - Problems



Optical Microscopy



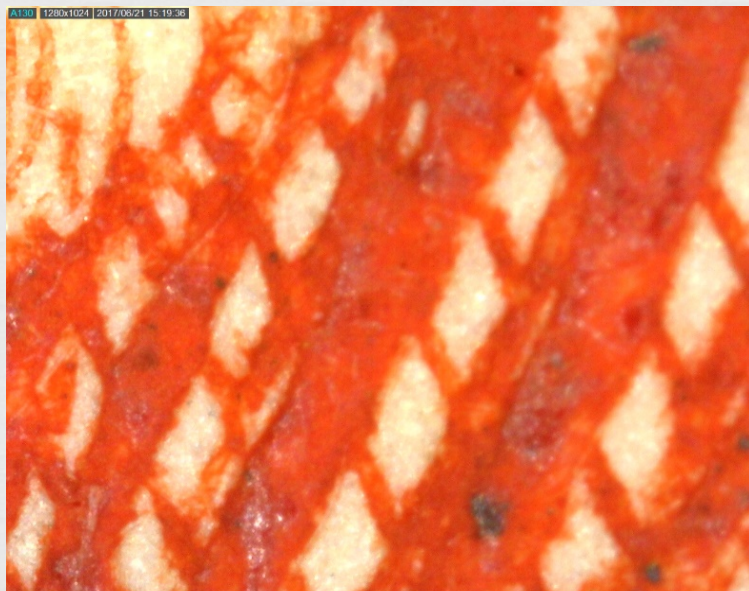
- ❧ The analysis was done with a Dino-Lite AM3113T optical microscope: 200x.
- ❧ The analysis was also done with an optical microscope generic brand: 1600x.



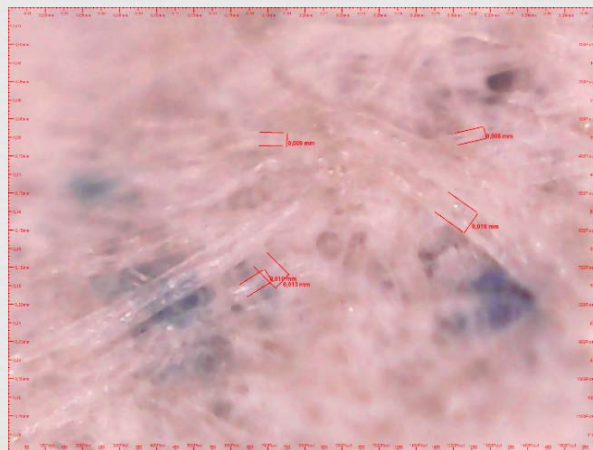
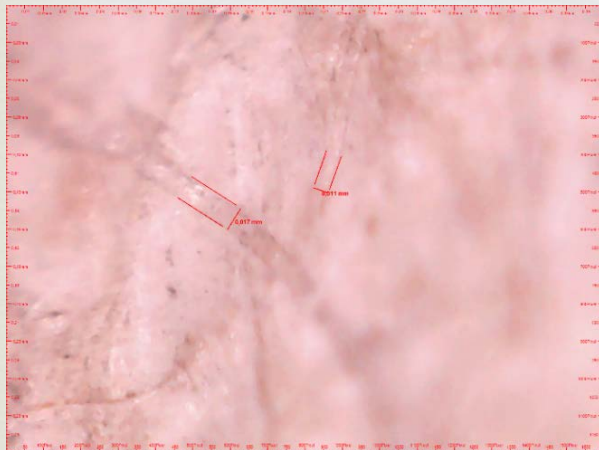
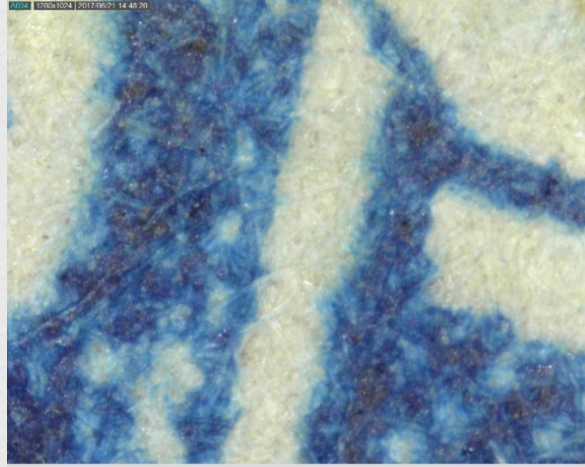
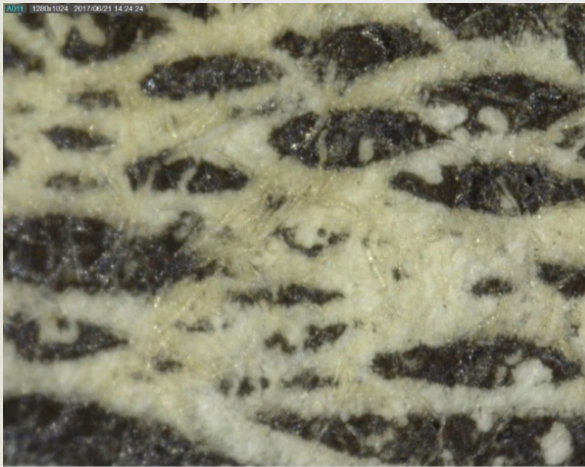
Engraved and Lithographed



- ✎ The imperial Brazilian stamps were engraved.
- ✎ The Cottens essays are engraved (1000 reis) and lithographed (2000 reis).
- ✎ Cottens essays in lithograph correspond to this Brazilian period: 1890s.



Fibres



Conclusions about the Paper



- ❧ The main conclusion reached is that the Cottens essay paper is a mixed fibres paper, which does not indicate the use of linter.
- ❧ The Cottens paper uses fine fibres with a thickness of 6 μm , which indicates the presence of wood fibres.
- ❧ The wood fibres were not common throughout the nineteenth century. The wood fibres began to be used from the 1880s (Katz).

Paper Thickness



❧ Carbon Fibre Composites Digital Thickness Caliper Micrometer Gauge.

❧ Problem:

❧ centesimal.

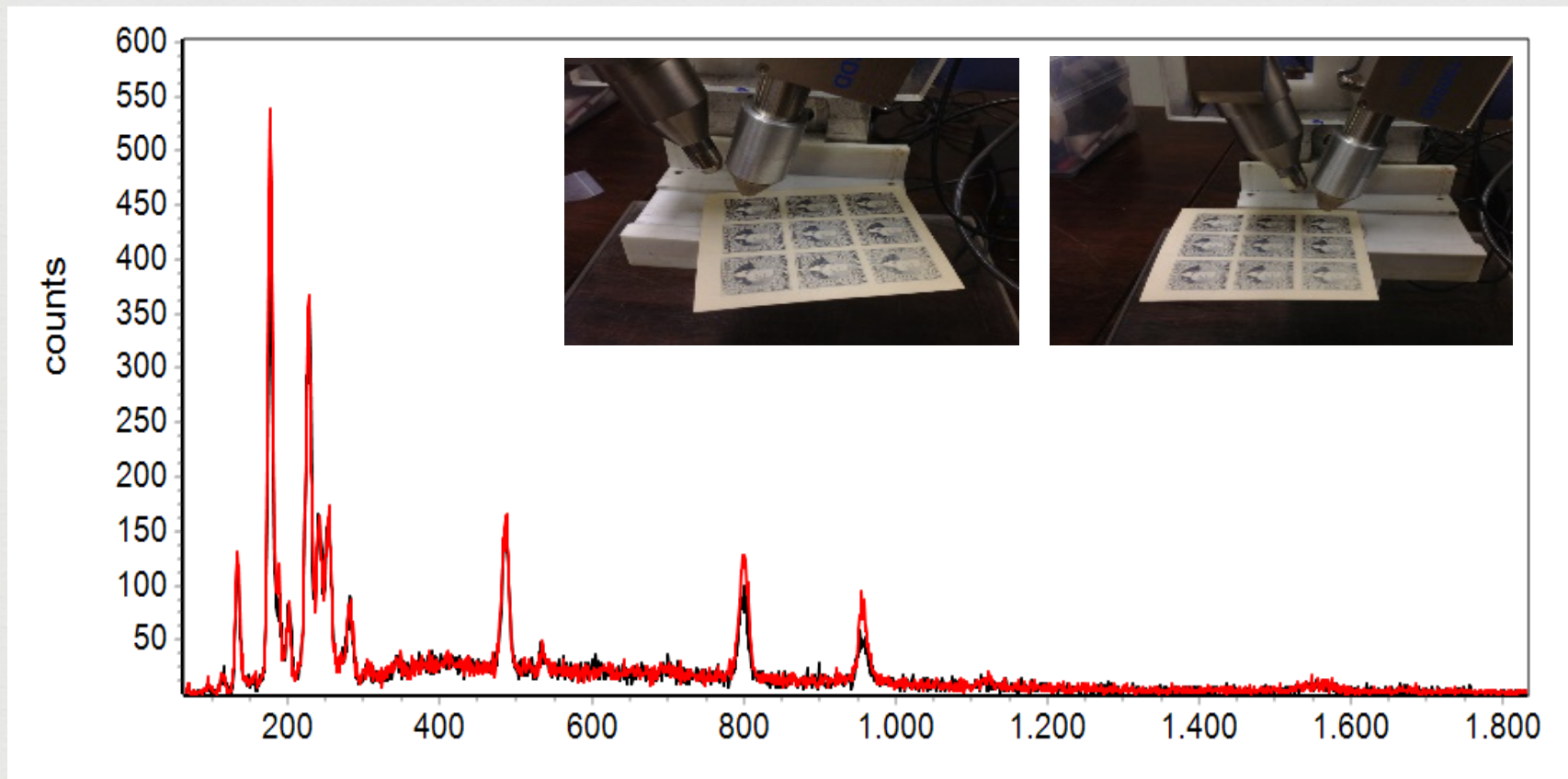


Paper Thickness of the Cottens Essays



Sample (Cottens Essays)	Paper thickness (microns)
Thin paper from the block	40-50 μm
1000 reis from the block / 2000 reis isolated	70-90 μm
Mix Essay	130 μm
Blue Paper 2000 reis	140 μm
Cottens Essay Isolated	150 μm
1000 reis Isolated Thick paper red	230 μm

Paper Thickness and Ink



Conclusions



- ✎ The analytical methods in philately allowed the creation of a database of the chemical elements present on Imperial Brazilian postage stamps.
- ✎ Due to the number of Brazilian stamps from the Empire and the number of variables regarding the paper and quantity of the pigments used in the inks, what is intended from the present study is to establish an initial database, but without exhausting the conclusions.
- ✎ Much more needs to be done in particular to analyze a larger number of each of the Brazilian stamps in a relevant quantity until the data is perfectly replicated for any sample.
- ✎ Significant conclusions were drawn from both the Brazilian stamps in general and the Cottens essays. The Cottens essays presented different patterns in relation to the pigments used by the studied issuers and their origin cannot be determined. The analytical studies did not corroborate previous historical studies.

About the Equipment



- ❧ The methods used were incomplete for the exact definition of the pigments used, but worked very well as an exploratory research in order to give guidance for future works.
- ❧ For the study of philatelic material it is possible to use XRF with the same efficiency of PIXE. The sensitivity of the PIXE analysis is not achieved in postage stamps.
- ❧ Other methods such as Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy may adequately complete the information required for the consolidation of this database for the Brazilian postage stamps.

Thank you!



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