Title: Characterization of 18th and 19th Century Postmarks from Peruvian Covers by Energy Dispersive X-ray Fluorescence and Raman Spectroscopy.

Objectives: The objectives of this research project were to determine the elemental and chemical composition of postmarks on 18th and 19th century Peruvian covers.

Introduction

Ink from the 18th and 19th century is composed of a vehicle, usually boiled linseed oil, with an inorganic or organic pigment. The number of inorganic pigments during this time was very, very few and is based on what was available on the local market. The local market could also reflect what was available in the country specifically dealing with mining activities. Many of these inorganic pigments can be described as being mineral earth pigments such as your iron oxides and mercury-based pigments. A popular and very old organic pigment that has been used for centuries is carbon black (C). In addition, organic dyes used in printing were derived from plant materials. For example Logwood and Brazilwood were common organic dyes used in inks during the 18th and 19th century. These dyes do not contain S. The ink maker would also incorporate a drier such as PbO (lead oxide) to make the ink dry faster.

Modern day organic pigments have replaced most of the toxic inorganic pigments that were used in inks from the 18th thru 20th century. These modern-day organic pigments are derived from coal tar (aniline). However, since these pigments contain only a few elements that can be detected by XRF, their identification can be determined by Raman.

Micro energy dispersive X-ray fluorescence (μEDXRF) was used to determine the elemental composition of the paper, writing text, and postmarks on 18th and 19th century Peruvian covers. In μEDXRF, a rhodium (Rh) X-ray tube was used to excite secondary x-ray fluorescence in the submitted samples. In addition, the instrument was configured with a poly-capillary lens to focus the X-ray beam down to 50-μ diameter. This allowed specific features of the covers to be analyzed such as paper blank, the writing text, and finally the postmark. It should be pointed out that EDXRF is non-destructive and there is no microscopic or macroscopic damage to the samples.

In EDXRF, the elements from sodium (Na) to uranium (U) are detected simultaneously. It only takes approximately 100 seconds to obtain a high quality EDXRF spectrum of a sample. This spectrum, as shown in Figure 1, provides the analysts with a qualitative elemental content of the item under analysis. From the spectrum, one can determine the relative amounts of each element in the analyzed sample. It should be pointed out that even though some peaks in the X-ray spectrum are higher than others, this does not mean that that element has a higher concentration than the other element. Also of note, most elements in the X-ray spectrum will have two peaks and there will always be several peaks from the Rh tube that appear in the spectrum. From an X-ray spectrum, software is used to determine quantitatively the concentration of the elements shown in the spectrum. For these analyses, it was not necessary to determine the concentrations of the elements in the samples. In addition, sometimes it is possible to determine the chemical composition of the pigment under analysis. For example, in the analysis of Cinnabar (HgS), the presence of mercury (Hg) and sulfur (S) in the X-ray spectrum (See Figure 1) can easily be interpreted as the pigment Cinnabar.

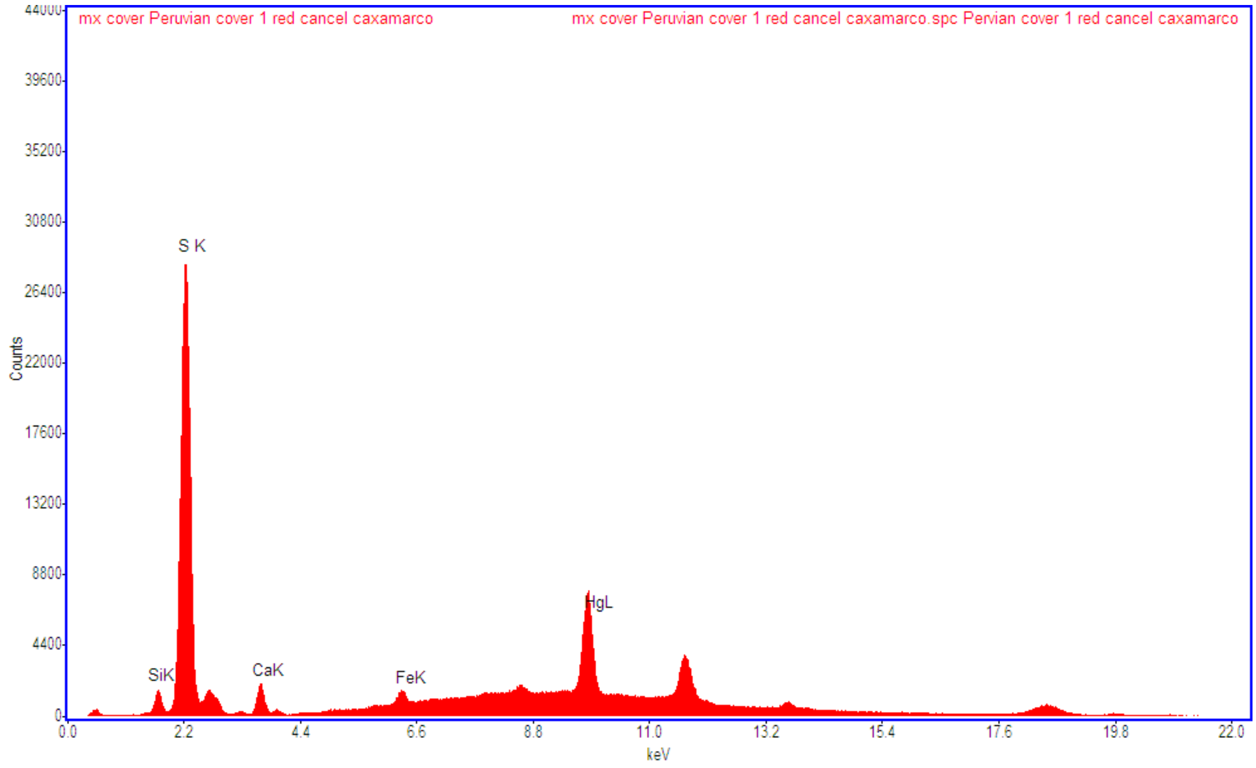

Figure 1. Representative X-ray spectrum of Caxamarco franca 1783 red postmark.

Experimental

My procedure to analyze the Peruvian covers was as follows:

1. I analyzed the paper blank,
2. I analyzed the written text,
3. and finally I analyzed the postmark.

For each of these spots, two locations were selected for analysis as shown in Figure 2.

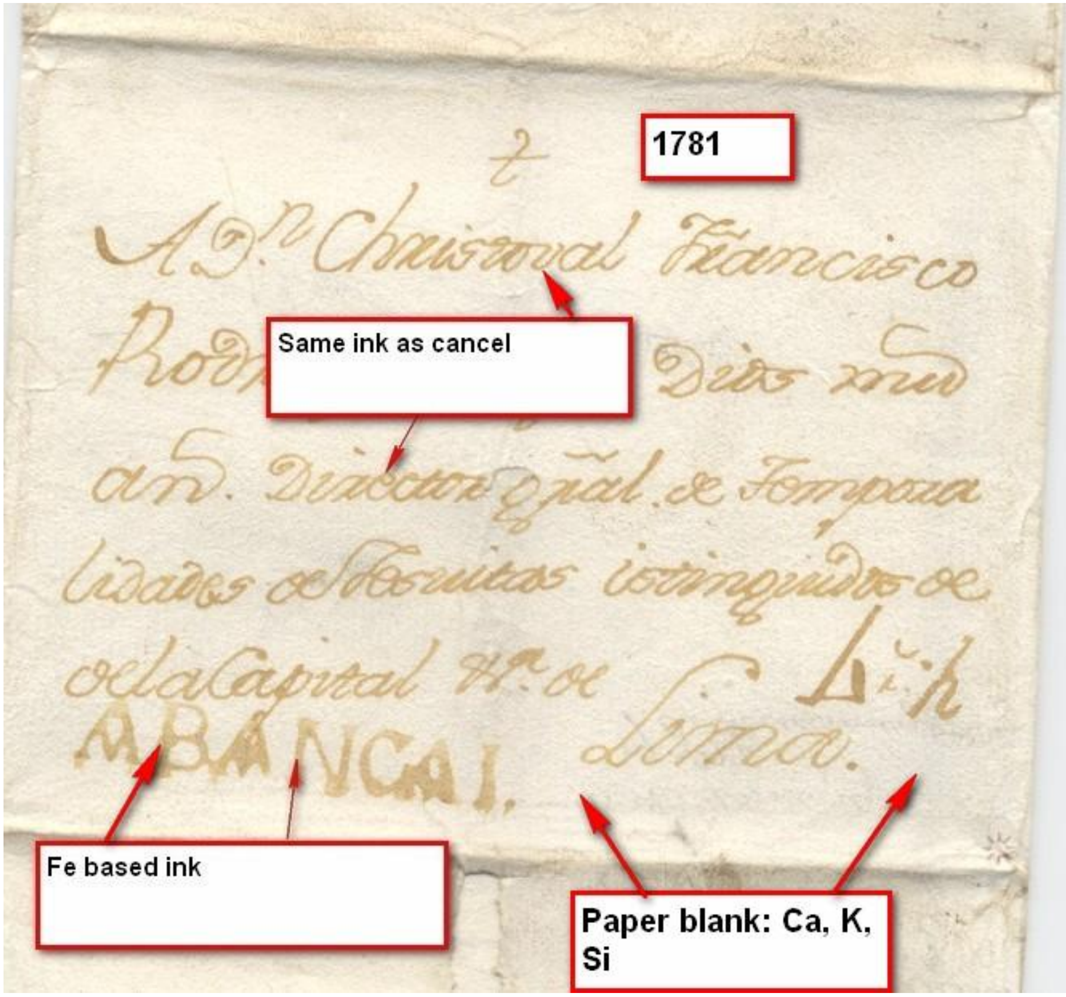

Figure 2. Typical µEDXRF and Raman sampling location map.

Therefore, my summary is based on the average of two analyses per feature in each of the Peruvian covers. It was very important to determine the elemental composition of the paper so that this information could be subtracted from the elemental composition of the postmark and the written texts so that correct interpretation could be used to explain the elemental composition in the postmarks.

After I analyzed the elemental content of the covers, I used Raman spectroscopy to determine the molecular composition of the ink. This way, the elements detected by EDXRF could be associated with specific chemical compounds. In Raman spectroscopy, I used a 785 nm (red) laser to scatter off of the postmark, paper, and postmark. Raman spectroscopy uses a 1-µ diameter laser beam to analyze specific features in the Peruvian covers such as paper, written text, and particles in the postmark. The Raman spectra could also assist in the determination of different crystal structures in the pigments used in the inks. By knowing the specific chemical compound, a tentative date on the printing of the inks could be ascertained. Also, there are numerous textbooks available that provide a chronology as to when different types of pigments were used in printing inks.

In addition, Raman spectroscopy is one of the few analytical techniques that can determine whether or not carbon Black was used in printing inks. Raman spectroscopy is also a non-destructive technique.

My procedure to analyze the Peruvian covers was as follows:

1. I analyzed the paper blank,
2. I analyzed the written text,
3. and finally I analyzed the postmark.

For each of these spots, two locations were selected for analysis as shown above in Figure 2. These locations were the same as those chosen in the EDXRF analyses.

A typical Raman spectrum of text ink is shown in Figure 3. Using my library of chemical compounds, pigments, and fibers, I can easily identify the various substances in a Peruvian cover. If a chemical compound is not in my library, the compound can still be identified based on general Raman scattering principles.

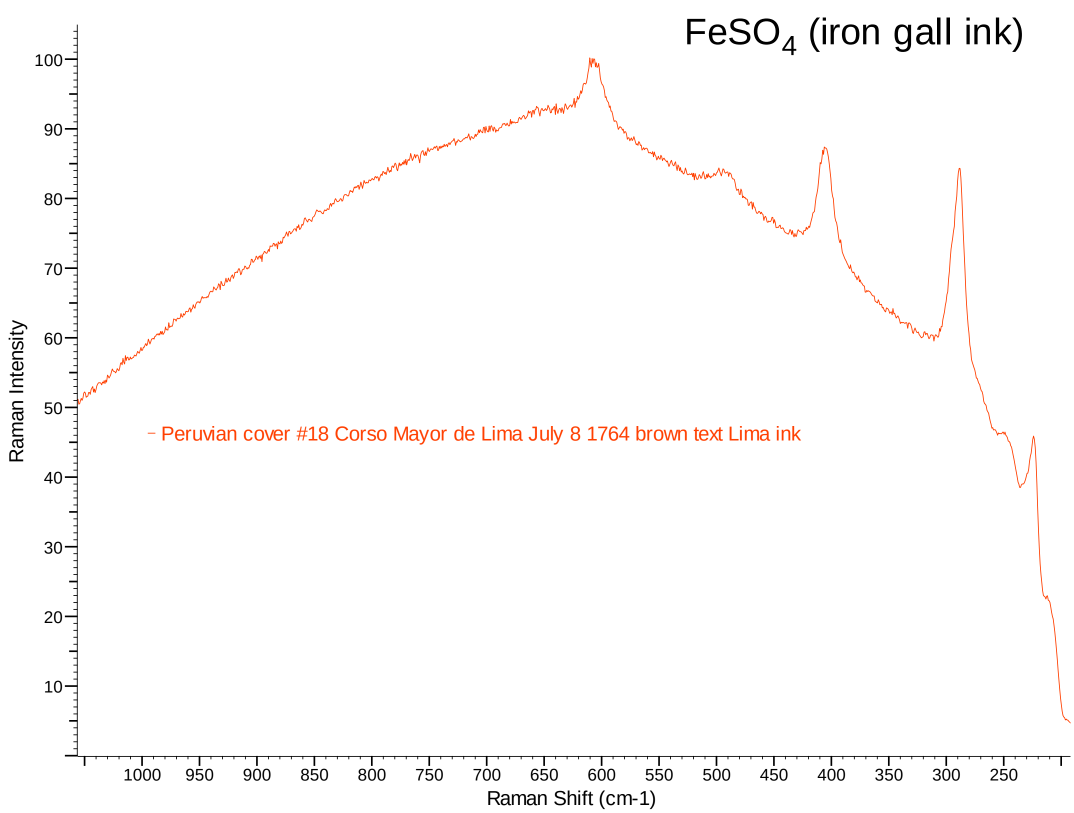

Figure 3. Raman spectrum of Corso Mayor July 8, 1764, brown writing ink.

I also supplemented the analyses with microphotography to look at the ink under high magnification (30X) to see ink particle structure and to determine if the ink separated. This can provide additional information on the authenticity of the ink and determine if there were overprints. Figure 4 shows a representative photomicrograph of one of the postmarks.

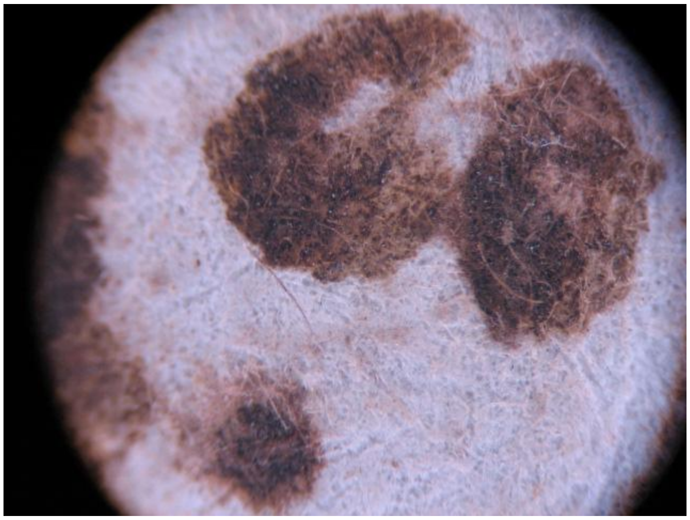

Figure 4. Photomicrograph of Santiago 1775 cover postmark.

Unfortunately these nondestructive analytical methods cannot be used to determine how long the ink has been on a document. However, if the pigment in the ink is oxidized, the original elements should still be present in the ink even if the original chemical compound has been transformed into another chemical compound. These elements are soaked into the cellulose paper fibers and still can be detected by XRF even if the ink is not visible. For example, if a sulfur-based ink contains iron (Fe gall ink, See Figure 5), if it is oxidized, the iron and sulfur should still be present in the x-ray spectrum. This was the method I used to recover erased text from the Archimedes Palimpsest.

From the 16^{th} to 19^{th} century, manuscripts were written using iron gall ink. This ink was made by mixing iron vitriol (iron(II) sulphate, $FeSO_4$) with gallnut extract. The black-brown, indelible iron (III) gallet complex was created following oxidization upon exposure to air (See Figure 5). Then, the Raman spectrum would show that the chemical compound has been transformed into another chemical compound.

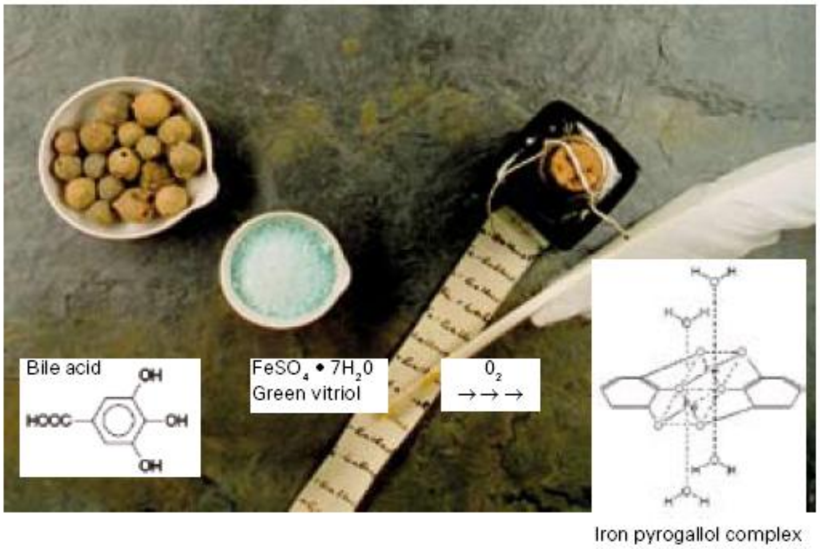

Figure 5. How Fe-gall ink is prepared. (From www.bruker.com).

Results and Interpretation

EDXRF revealed that the composition of most of the red postmarks is composed of either the mineral cinnabar (HgS) or red lead (Pb_3O_4, or $2PbO{\cdot}PbO_2$). These pigments are consistent with the time period when the covers were postmarked. The elemental and chemical composition of all the postmarks is summarized in Table 1 attached. Some of the black inks contained high concentrations of sulfur with no other accompanying elements (Na to U). Because S was found by itself in the black postmarks suggest that the pigment is an organic base pigment made from aniline. Traditionally, black ink from this time period would have usually been composed of the pigment carbon black as was shown on a few of the other black postmarks as was determined by Raman spectroscopy. Therefore, this black ink containing sulfur is a modern day aniline dye that was synthesized and available for making inks after the 1900's.

The brownish-red postmarks were identified as iron-ball ink. The pigment found in the Abancai 1781 brownish-red cancel was identical to that of the hand-written text. (See Figure 2 above).

Overall, most of the pigments in the postmarks on the Peruvian covers are consistent with the pigments available in the 18th and 19th century. Only those black postmarks containing S alone are suspect and are not consistent with pigments available in the 18th and 19th century. None of these postmarks appear on your list "undisputed covers, believed authentic by everyone." Also of curiosity is the appearance of overprinting of some postmarks as shown in Figure 4 above and Figure 6 below.

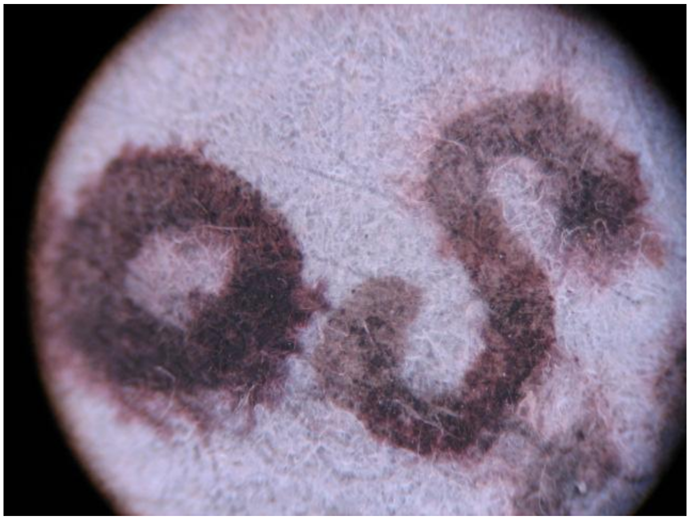

Figure 6. Photomicrograph of Coreo Potosi 1765 postmark that contains high S.

Prepared 24 July 2010 by

Gene S. Hall, Ph.D.

Professor of Analytical Chemistry

Department of Chemistry and Chemical Biology

Rutgers, The State University of New Jersey

New Brunswick, NJ 08903

Cover	Year	Ink color	Elements	Pigment	Time Period
Passaporte 1750 cancel p1	1750	black	High S	?	unknown
Passaporte 1750 cancel p2	1750	black	High S	?	unknown
Coreo mayor Huamanga 1752 cancel ink p1	1752	black	High S	?	unknown
Coreo mayor Huamanga 1752 cancel ink p2	1752	black	High S	?	unknown
Santiago 1755 black cancel p1	1755	black	High S	?	unknown
Santiago 1755 black cancel p2	1755	black	High S	?	unknown
Coreo Potosi 1765 cancel	1765	black	High S	?	unknown
Coreo Potosi 1765 cancel pos 2	1765	black	High S	?	unknown
Lima 1771 black cancel p1	1771	black	C	carbon black	correct
Lima 1771 black cancel p2	1771	black	C	carbon black	correct
Guancavelica 1773 red cancel	1773	red	Hg, S	HgS	correct
Guancavelic franca 1774 red cancel p2	1774	red	Hg, S	HgS	correct
Guancavelica franca 1774 red cancel	1774	red	Hg, S	HgS	correct
Truxillo Franca 1777 cancel red	1777	red	Pb	Pb_3O_4, or $2PbO \cdot PbO_2$	correct, red lead
Balparaiso 1778 brown cancel p1	1778	brown	Fe, S	$FeSO_4$ (iron gall)	correct
Arequipa 1778 red cancel p1	1778	red	Hg, S	HgS	correct
Cuzco 1778 cancel	1778	black	High S	?	unknown
Jauja 1780 black cancel p1	1780	black	C	carbon black	correct
Jauja 1780 black cancel p2	1780	black	C	carbon black	correct
Abancai 1781 red cancel	1781	red	Fe, S	$FeSO_4$ (iron gall)	correct
Abancai 1781 red ink cancel p2	1781	red	Fe, S	$FeSO_4$ (iron gall)	correct
Palpa Franca 1781 cancel 1 FRANKA	1781	black	Fe, S	$FeSO_4$ (iron gall) or FeS	correct
Palpa Franca 1781 cancel 2 Palpa	1781	black	Fe, S	$FeSO_4$ (iron gall) or FeS	correct
Caxamarco franca 1783 red cancel	1783	red	Hg, S	HgS	correct
Coreo Mayor de Lima 7-8-1794 black cancel	1794	black	High S	?	?
Pasco 1810 red cancel	1810	red	Pb	Pb_3O_4, or $2PbO \cdot PbO_2$	correct, red lead
Pasco 1810 red cancel p2	1810	red	Pb	Pb_3O_4, or $2PbO \cdot PbO_2$	correct, red lead
Camana sin fecha cancel	?	brown	Fe, S	$FeSO_4$	correct
Camana sin fecha cancel p2	?	brown	Fe, S	$FeSO_4$	correct

Comment
similar ink
similar ink
similar ink
similar ink
cinnabar r
cinnabar r
cinnabar r
same ink a
cinnabar r
same ink a
same ink a
cinnabar r
iron galls
iron galls