

## Analysis of 19th century Mexican postage stamps by PIXE

Thomas E. Gill

*University of Texas at El Paso, Department of Geological Sciences, El Paso, Texas 79968, USA*

**Abstract.** Subtle variations in ink color and paper of postage stamps can affect their value and desirability to collectors and investors. PIXE has been utilized since the mid-1980s in studies of inks and papers used for postage stamp printing. Almquist (1985) utilized PIXE to analyze the paper and the color of blue and green inks on 1887 Mexican “Numerals” stamps, revealing color variations apparently related to metal content. Mexico’s 15-centavo Mail Transportation stamps of 1895- 1898 (“Multas”) were printed in varying color shades from bluish to greenish, believed to be from the same ink type as the “Numerals”. External beam PIXE milliprobe was used to analyze paper and ink of examples of the “Multas” to investigate whether similar printing variations would be revealed. Elemental differences between the “Multas” and “Numerals” stamps and between bluish and greenish “Multas” color shades were noted. The “Multas” papers were relatively devoid of inorganic fillers and binders used in the “Numerals” paper. Unlike the “Numerals” stamps, the “Multas” ink apparently was primarily organic (predating previously-known use of non-metallic ink in Mexican stamp printing) with minor amounts of metals including titanium, zinc, and lead. “Multas” color variations from greenish to bluish are related to metal content, with more zinc and lead in the first, bluish printing and more titanium in the last, greenish printing. Different batches of pigment appear to have been used for each printing, with color differences apparently related to the presence of sulfur compounds and the addition of metal oxide whiteners.

**Keywords:** Archaeometry, ink, paper, stamps, Mexico.

### INTRODUCTION

Since their introduction in 1840, postage stamps have been acquired as collectibles and investments, and studied to reveal information on the history of printing. Variations in ink and paper of otherwise identical-appearing stamps may affect their value and desirability to collectors and investors. Due to its ability to nondestructively reveal elemental composition, PIXE is an applicable technique for analysis of historical inks and papers, and has been used on postage stamps since its early days (1,2,3,4,5).

The late H.J. Almquist utilized PIXE (1) to determine that variations in color from bright blue to bright green on the Mexican “Numerals” stamps printed in 1887 (Figure 1) were associated with composition of the ink, especially variations in metal content. He noted that color variations were known ranging from bluish-green (believed to be from earlier printings) to greenish-blue (believed to be from later printings) on the 15-centavo “Multas” stamp of the

Mail Transportation set printed by Mexico from 1895-1898. Some studies of variations in the paper of these stamps had been done (6), but not of the ink. This motivated the current work.



**Figure 1.** Bright green “Numerals” stamp.

### MATERIALS AND METHODS

Analyses were performed at the Crocker Nuclear Laboratory at the University of California, Davis (UCD), with an external-beam (in air) PIXE proton

milliprobe. The PIXE analytical setup is well described in references 7 and 8, and summarized here. The isochronous cyclotron at UCD produces a beam of 4.5 MeV protons which is taken into air, passes through the sample generating X-rays, and is collected in a Faraday cup. The beam was collimated to a 1.0 by 0.5 millimeter area for these analyses, and laser-aligned to irradiate a specific spot on the sample. A Si(Li) energy-dispersive detector placed several centimeters from the sample, presenting a large solid angle (5,7), was used for X-ray detection and spectrometry. Count rates were on the order of ~700 to 1500 Hz for the samples analyzed here. A NIST thin film multielemental standard SRM-1533 was also analyzed during the run to ensure that reported concentrations were accurate.

Eight of the “Mulitas” stamps were obtained, four each in distinctly bluish and greenish color shades (Figure Set 2). A dark area of solid ink near the top frame of each stamp (away from any cancellation mark) was analyzed, as well as a portion of the unprinted paper in the margin of each stamp. Each spot was exposed to the beam for 100 seconds. Prior analyses of other papers and inks on other historical documents under these conditions (7,8) had not been reported to cause any noticeable damage to samples, and no discoloration or other observable damage to the stamps was caused by these analyses.



**Figure Set 2.** The 15-centavo Mexico “Mulitas” postage stamp, bluish shade (left) and greenish shade (right). Images are of two of the actual stamps analyzed.

## RESULTS AND DISCUSSION

Nine elements were detected (Figure Set 3), only three at levels exceeding  $1 \mu\text{g}/\text{cm}^2$ : Zn, Si, and S. Six elements were detected at lower levels: Ti, Pb, V, Cl, Ca, and Fe.

Distinct differences in elemental composition between bluish and greenish inks of the “Mulitas” were noted, as were differences between the “Numerals” and “Mulitas” inks and papers.

Unlike the “Numerals” stamps analyzed by Almquist (1, 9: Figure 1), which were apparently printed with K-Fe based, Cr-bearing inks on papers with clay (Mg, Si, Al, Ca) coatings/fillers, the absence or reduced levels of these elements in the “Mulitas” stamps suggests they may have been printed with organic-based inks on papers largely devoid of clay additives. This and the presence of S suggests that Mexican stamps were printed with aniline (sulfone-derived organic) pigments earlier than 1899, as had been previously thought (6). Chinese stamps also issued in 1895 were also determined by PIXE to have been printed with predominantly organic inks (3). The “Mulitas” paper is harder and stronger than the “Numerals” paper, which was easily torn probably due to its clay additives. It is noticeably lower in Ca than other types of papers from the eighteenth century investigated in early PIXE analyses (5).

Zn, Pb and/or Ti oxides or hydroxides were often added to Mexican (1, 9) and other (2, 3) stamp ink pigments of the era as brighteners, lighteners or extenders. Their presence in the “Mulitas” inks and depletion in papers suggests their use modulated the color shades of the stamps: bluish inks having more Zn and Pb, greenish inks having less. These elements may have either directly influenced the shade of the ink as printed, or secondarily protected against a post-printing color change perhaps associated with the presence of S in the inks.

Variations in the areal concentrations of individual elements in the ink from stamp to stamp could be caused by varying amounts of ink transferred to the stamp in the printing process. However, elemental ratios in the ink applied to each stamp should remain similar. This can be seen in Figure 4, for Pb/Ti. That the two lines extrapolate to near zero suggests these mixes were the principal sources of these elements. The two distinct Pb/Ti ratio lines suggest different mixes of brighteners (different batches of inks) were associated with the bluish and greenish shades.

## CONCLUSIONS

Several observations can be made with these limited data. PIXE continues to be a useful technique for the nondestructive testing of the papers and inks of postage stamps. It appears from the analyses that the 1895- 1898 “Mulitas” stamps, unlike the previous Mexican issues, were printed with organic-based inks on largely clay-free papers. Mexican stamps may have been printed with organic inks several years earlier than previously known. Differing amounts and/or formulations of metal (Zn, Pb, Ti) oxide whiteners apparently controlled the present-day color shade of the stamps, either directly or indirectly, with bluish

inks having relatively more Zn and Pb, and greenish inks having relatively more Ti.

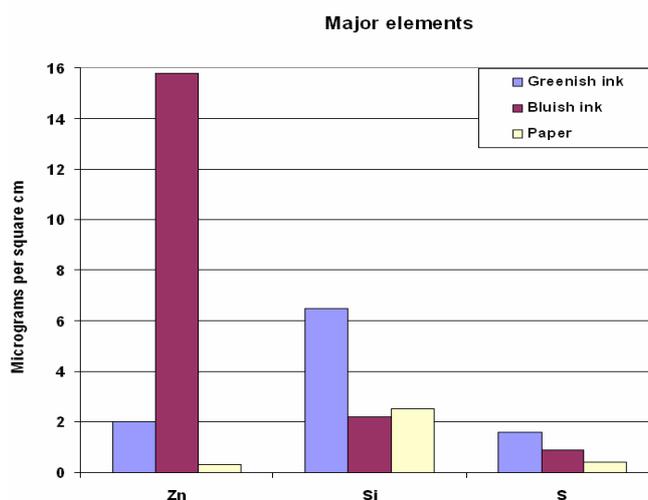
## ACKNOWLEDGMENTS

This study is dedicated to the late H.J. Almquist (1903 – 1994), who inspired the investigation. Thanks are given to T.A. Cahill and others at Crocker Nuclear Laboratory, University of California- Davis, for analytical assistance.

## REFERENCES

1. H.J. Almquist, *American Philatelist* **99** (1985) 241- 242.
2. E.M. Johansson *et al.*, *Nucl. Inst. and Meth.* **B14** (1986) 45- 49.
3. G.S. Hall and M.L. Lee, *Nucl. Inst. and Meth.* **B49** (1990) 573- 576.
4. H. Cheng *et al.*, *Nucl. Inst. and Meth.* **B136-B138** (1998) 897- 901.
5. T.A. Cahill *et al.*, *Nucl. Inst. and Meth.* **181** (1981) 205- 208.

6. K.H. Schimmer and C.P. Bulak, *Mexicana*, January 1972, pp. 1- 40.
7. T.A. Cahill *et al.*, *Anal. Chem.* **59** (1987) 829- 833.
8. B.H. Kusko and R.N. Schwab, *Nucl. Inst. and Meth.* **B22** (1987) 401- 406.
9. H.J. Almquist, *Mexicana*, October 1986, pp. 207- 208.



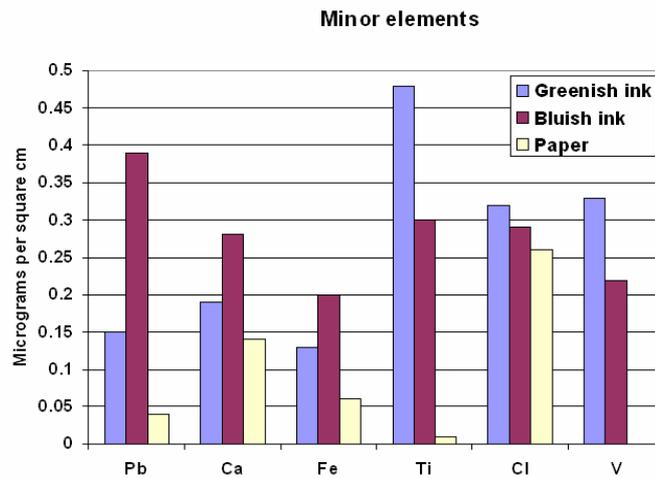


Figure Set 3. Elements detected in the “Mulitas” stamps ink and paper.

### Lead vs. Titanium

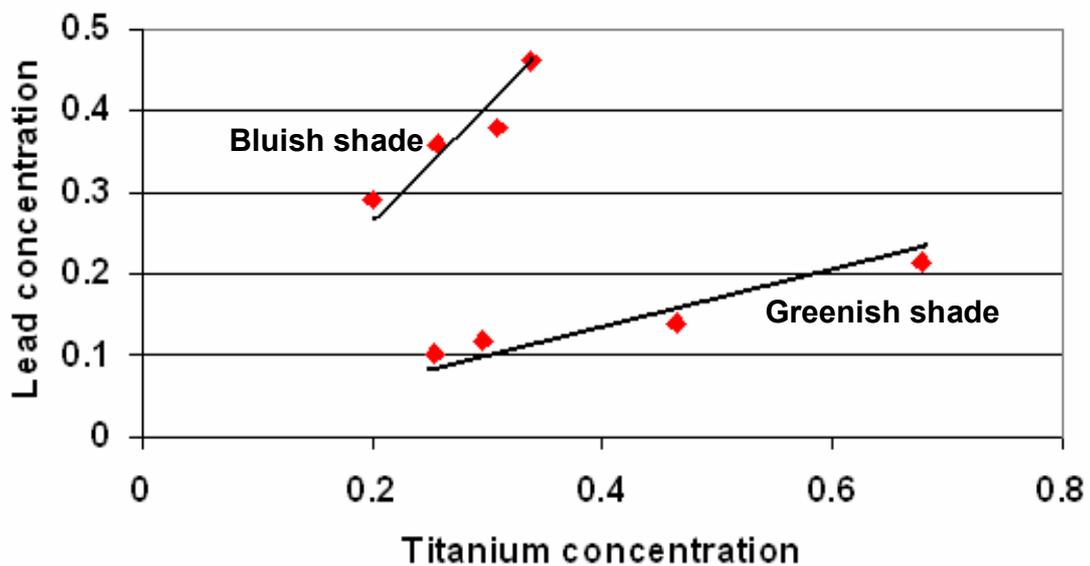


Figure 4. Pb/Ti ratios in the two different color shades of the “Mulitas” stamps analyzed by PIXE. The two Pb/Ti ratios suggest two sources or batches of ink brighteners/extenders, for the bluish (higher Pb) and the greenish (lower Pb) inks. Values in micrograms per square centimeter.