

A Scientific Analysis of the First Issues of Chile 1853–1862, London Printing

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ABSTRACT. The London printings of the Chilean postage stamps between 1853 and 1862 were examined using analytical instruments available at the Smithsonian Institution. There are four broad major technical areas important to philatelic research: color science (colorimetry and luminescence), paper chemistry (composition, thickness, and roughness), ink chemistry (pigment and binder composition), and printing methods (engraving and lithography). The analyses performed in this study address these four broad major technical areas while providing an understanding of the characteristics of these stamps, showing the utility and capability of forensic and scientific equipment available to philatelic researchers and offering an effective, rapid, and nondestructive way of identifying the pigments and dyes in the inks and papers used. X-ray fluorescence (XRF), Fourier transform infrared spectroscopy (FTIR), colorimetry, and X-ray diffraction (XRD) were all used on the stamps without damaging the samples. In some cases different XRF and FTIR manufacturers were used to compare the capabilities of different instruments in analytical philately. Because of the significant sensitivity differences of the equipment, the results are often complementary. Only by combining the results from several pieces of equipment was it possible to gather enough information to fully differentiate between the stamps and to obtain the complete characterization for each ink, pigment, and paper. This paper gives guidance as to which scientific instruments and methods are most useful when examining different characteristics of stamps. The results show the inks vary considerably between different printings. In the various red inks used by Perkins, Bacon & Co. the variation in the amounts of iron, calcium, and potassium used in the stamps examined show printer experimentation in the recipe used to make the ink. However, comparison between two blue inks used between 1853 and 1862 show little variation in the components used. This suggests much of the variation in the red ink recipe is due to Perkins, Bacon & Co. trying to solve the bluing problem present in many of their stamps during this time period.

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INTRODUCTION

Using different pieces of scientific/forensic equipment at the Smithsonian National Postal Museum (NPM) and Smithsonian Museum Conservation Institute (MCI), this study focuses on the London printings of the Chilean postage stamps issued between 1853 and 1862.

STAMPS AND PAPER

A listing of the Chilean stamps is given below (Scott Publishing Co., 1997).¹

- First London Printing, July 1853
 - 5 centavos brown-red on blued paper (Chile number 1)—issued 300,000 stamps
 - 10 centavos deep bright blue on yellowish-white paper (Chile number 2)—issued 200,160 stamps
- Second London Printing, May 1855
 - 5 centavos brown-red on blued paper (Chile number 8)—issued 2,040,000 stamps
- Third London Printing, October 1861
 - 10 centavos bright blue on yellowish-white or lightly blued paper (Chile number 12)—issued 3,000,000 stamps
- Third London Printing, 1 January 1862
 - 1 centavo lemon yellow on yellowish-white paper (Chile number 11)—issued 3,000,000 stamps
 - 20 centavos green on yellowish-white paper (Chile number 13)—issued 3,000,000 stamps.

Four major technical areas are important to philatelic research of the Chile stamps: color science (colorimetry and luminescence), paper chemistry (composition, sizing, thickness, and roughness), ink and gum chemistry (pigment and binder composition), and printing methods (engraving and lithography). The analyses performed in this study address these four major areas while providing an understanding of the characteristics of these stamps, showing the utility and capability of forensic and scientific equipment available to philatelic researchers and offering an effective, rapid, and nondestructive way of identifying the pigments and dyes in the inks and papers used.

X-ray fluorescence (XRF), Fourier transform infrared spectroscopy (FTIR), colorimetry, and X-ray diffraction (XRD) were all used on the stamps without damaging the samples. In some cases (XRF and FTIR) multiple instruments used the same analytical technique to further explore the capabilities of different instruments in analytical philately and of the significant sensitivity differences of the equipment, and the results are often

complementary. Only by combining the results from several pieces of equipment was it possible to gather enough information to obtain the complete characterization for each ink, pigment, and paper. This paper gives guidance as to which scientific instruments and methods are most useful when examining different characteristics of stamps.

HISTORY

On 14 June 1852, Messrs. Lyon Brothers, agents for the Chilean government, sent a letter from Valparaiso to Perkins, Bacon & Co. on behalf of the Chilean government. The letter contained an order for postage labels (stamps): 300,000 five centavos printed in red vegetable ink and 200,000 ten centavos printed in blue vegetable ink, as well as the original steel printing plates, 100 reams of watermarked paper, one gross obliterating hand stamps, and one dozen bottles of obliterating ink (Bacon, 1902; De Worms, 1953; Gálvez, 1964; Blank, 1989; *Chile the "Colon" Issues*, 2011; Granzow, 2012).

On 31 January 1854, a second printing was ordered for an additional 2,040,000 five-centavos postage labels printed in red vegetable ink, 100 pounds of gum, the printing plate, and a printing press with complete instructions on how to apply the ink and use the press (De Worms, 1953).

The third and final order was received by Perkins, Bacon & Co. on 8 December 1859 for 3,000,000 postage labels of 1 centavo printed in yellow vegetable ink, 10 centavos in blue vegetable ink, and 20 centavos in green vegetable ink. The four different value stamps printed by Perkins, Bacon & Co. are shown in Figure 1.

Included in the shipment to Valparaiso were the steel printing plates, reams of watermarked paper, 56 pounds of red vegetable ink, 30 pounds of blue vegetable ink, 25 pounds each of green and yellow vegetable inks, and 250 brass canceling devices with the word "CANCELLED" located between four straight lines (De Worms, 1953). Although the printed stamps and supplies left London in September 1860, the 10-centavo stamp was issued for postal use in October 1861, and the 1-centavo and 20-centavo stamps were issued on 1 January 1862.



FIGURE 1. Chile first issues—the London printings (left to right: Scott numbers 1, 2, 8, 11, 12, and 13).

Perkins, Bacon & Co. inks were typically composed of two parts, a liquid and a dry pigment. The liquid portion was referred to as “oil,” as it was made by heating linseed oil and beeswax until slightly burned. This provided a carrier or varnish for the pigment. To this mixture “soft soap,” which helped to disperse the pigment and turpentine, was added to thin the oil to the desired viscosity. One or more dry pigments or colorants were mixed into the oil to form the final ink (Bacon, 1920b:181).

Many of the Perkins-Bacon inks were cyanide based. Six colorants can be made by the reaction of iron with the carbon-nitrogen radical ($-C \equiv N$), cyanide: Prussian yellow, Prussian red, Prussian blue, Chinese blue, Prussian green, and Prussian brown (Granzow, 2012).

MICROMETER

A micrometer can calculate the exact thickness of a sheet of paper or a printed stamp. The paper used for the Chile stamps was handmade; due to the human element, one sheet of handmade paper differed from the next in thickness. Such variation in thickness is expected because, in the 1840s in Great Britain, paper was sold by weight per ream. “The supplies of the watermarked paper furnished to Perkins, Bacon & Co. under Mr. Stacey Wise’s contract, were made in triple sheets ($31 \frac{1}{2}$ by $59 \frac{1}{4}$ inches), and every sheet was divided into three parts before it was used for printing the stamps. The three divisions of the sheet when cut each measured $10 \frac{1}{2}$ by $19 \frac{3}{4}$ inches. The weight per triple ream was $31 \frac{1}{2}$ lbs, one ream equaling 500 sheets” (Bacon, 1920a:40–43).

COLORIMETRY

The use of colorimetry in philately has been discussed in depth in a recent article by Herendeen et al. (2011) and Allen and Lera (this volume).

X-RAY FLUORESCENCE

Nondestructive X-ray fluorescence (XRF) analysis is one of the most widely used and versatile of all instrumental analytical techniques. An XRF spectrometer uses primary radiation from an X-ray tube to excite secondary X-ray emission, or fluorescence, from a sample. The energy (in kV) of the fluoresced radiation is used to identify the chemical element from the sample that emitted the X-ray. For a very X-ray dense material, for example, a metallic alloy, the XRF spectrum penetrates only a few micrometers into the sample. For stamps, however, it should be expected the XRF spectrum will include elements from all the layers of the stamp: ink, cancellation, paper, gum, and any residual backing material. The height and area of each X-ray peak, measured in counts, relates to the concentration of the element in the sample. For further background on X-ray fluorescence see reviews by Hahn et al. (2006) and Janssens et al. (2000). XRF has been used on stamps

before, both alone and in conjunction with other techniques, to study the materials used in the manufacturing of the stamps as well as to identify counterfeits (Sanchez and Valentinuzzi, 2006; Castro et al., 2008; Cesareo and Brunetti, 2008; Preiss and Robie, 1982).

INFRARED SPECTROSCOPY

Fourier transform infrared (FTIR) spectroscopy refers to the manner in which the data are collected and converted from an interference pattern to an infrared spectrum and is used for the identification of organic as well as inorganic materials. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. For most common materials, the spectrum of an unknown can be identified by comparison to a library of known compounds (Griffiths and de Haseth, 2007; Infrared and Raman Users Group, 2013).

A common method of acquiring IR spectra is using attenuated total reflection FTIR (ATR-FTIR). When using ATR-FTIR, the sample must be in complete contact with the ATR window, which frequently involves applying pressure to the sample. The infrared light in ATR-FTIR penetrates a small amount into the sample; the depth of penetration in ATR-FTIR is greater than the thickness of the ink, so information on both the paper and ink will be present in an ATR-FTIR spectrum. ATR-FTIR produces slightly different spectra when compared to the standard transmission spectra in an infrared library. ATR spectra can be easily corrected, if desired, before comparing to an IR library. Because of the small size of postage stamps, ATR-FTIR can generally be used without requiring a sample to be extracted from the stamp or any modification of the instrument. For more background on infrared spectroscopy see Derrick et al. (1999). Infrared spectroscopy has been used previously to examine the ink used in stamps; however, most of the data came from ink samples removed from the stamps (Ferrer and Vila, 2006).

X-RAY DIFFRACTION

Powder X-ray diffraction (XRD) is perhaps the most widely used X-ray diffraction technique for characterizing materials and examining the crystalline structure of compounds. Although this technique is typically thought of as useful for inorganic materials, some organic materials are also quite crystalline and can give identifiable X-ray diffraction data. As with infrared spectroscopy, X-ray diffraction data are generally compared to a library of known reference materials to identify the compounds that produced the peaks.²

MATERIALS AND METHODS

STAMP SELECTION

Because of security issues with moving the Bernard Peyton Collection of Chile (accession number 223486)³ out of the NPM,

analysis of the author's private collection was performed using forensic equipment at MCI.

VIDEO SPECTRAL COMPARATOR 6000

Optical examination was completed using the NPM's Video Spectral Comparator 6000 (VSC 6000) manufactured by Foster + Freeman, Ltd. in Evesham, Worcestershire, United Kingdom (Figure 2). The VSC 6000 allows examination of the stamps using incident and transmitted visible and near-infrared illumination between 400 and 1000 nm.

Twenty Chile stamps of each issue were tested. Each stamp was placed in the VSC 6000 and enlarged using a magnification factor of 8 so the sensor area (represented by crosshairs) was able to average the color over a 0.2 mm² area (Figure 3). Three inked points were sampled on each stamp. If the stamp was canceled, an attempt was made to sample "pure" color, that is, a region with no apparent white or black.

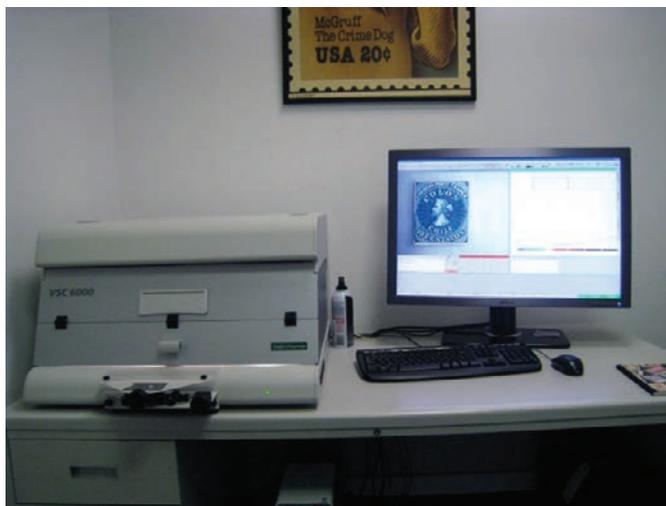


FIGURE 2. Video Spectral Comparator 6000 (VSC 6000).



FIGURE 3. Sampling point on Chile number 12.

For each of the three points, the spectral reflectance curves were plotted to verify the readings, yielding consistent results. During the data collection procedure, a visual inspection of each graph was made to insure no highly inconsistent measurements were obtained. In the event inconsistent data were recorded, one or more of the data points for the sample would be retested. These data points were averaged and used in the following analysis.

For each of the samples, a full range of colorimetry data was collected and reviewed, including chromaticity diagrams (both CIE 1931 and CIE UCS 1960). All tabular data, including tristimulus values, CIE 1931 x, y coordinates, CIE UCS 1960 u, v coordinates, and CIE UCS 1976 $L^*u^*v^*$ coordinates, were collected.

At the time of the analysis, the VSC 6000 did not support CIE 1976 u', v' chromaticity coordinates. The measured tristimulus values (X, Y, Z) were used to compute these coordinates using the standard transformations (Herendeen et al., 2011; Herendeen, 2011):

$$u' = \frac{4X}{X+15Y+3Z} \quad v' = \frac{9Y}{X+15Y+3Z}$$

On 14 November 2012, the software program was updated to version 160 to calculate these values.

OTHER COLORIMETRIC ANALYSIS

Concurrently with the colorimetric analysis, James Allen, a recognized philatelic color expert, categorized all of the stamps in a controlled environment illuminated with a 5000 K daylight source. Stamps were held at a constant angle of inclination with respect to the light source.

PAPER THICKNESS

The Testing Machines Inc. model 49-76-01, a precision micrometer suitable for measuring thin sheet materials—paper, tissue paper, and cardboard (Figure 4)—at the NPM, was used to measure the thickness of the stamp. The measuring range of the micrometer is 0.000–1.250 mm with a resolution of 0.1 μm and an anvil diameter of 1.59 cm (0.68 inches) with a contact pressure of 7.3 psi. It conforms to Technical Association of the Pulp and Paper Industry (TAPPI) T-411 standards. The micrometer has a large digital display, auto zero, motorized auto cycling, and a serial port for data communications to graph master software with the results exported to a Microsoft Excel spreadsheet.

MICROSCOPY

The Leica microscope model M205C, with magnification range from $\times 78$ to $\times 1,600$, was used in conjunction with the VSC 6000 software to record close examination details (Figure 5).

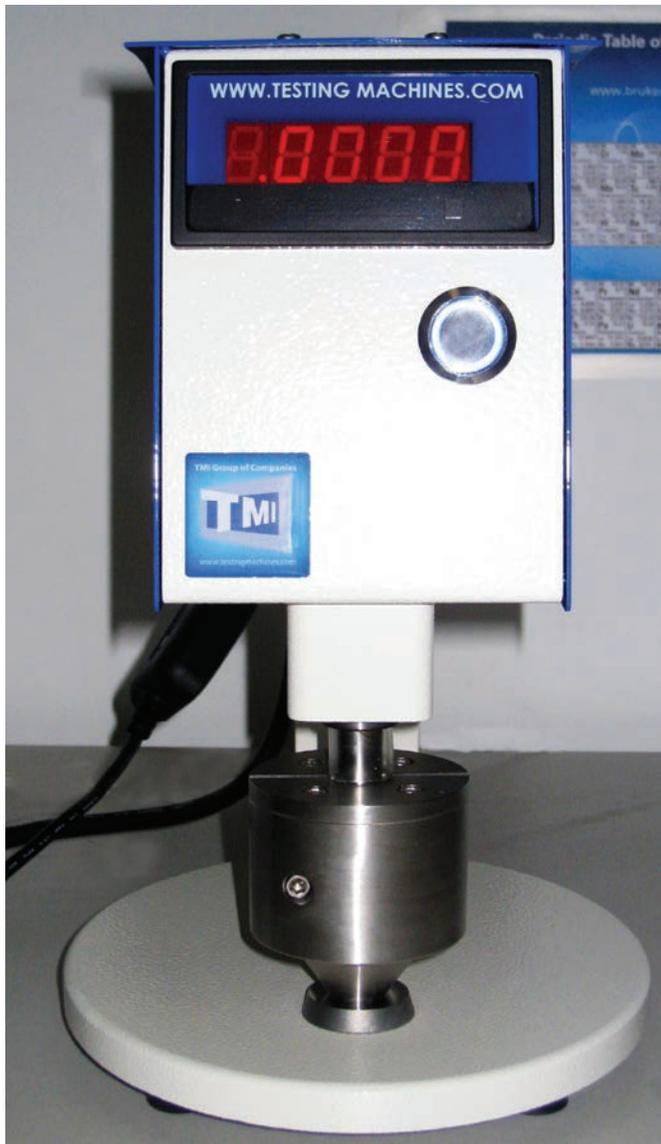


FIGURE 4. Testing Machines Inc. model 49-76-01 micrometer.

X-RAY FLUORESCENCE

Two instruments were used for XRF of stamps in this project. At the NPM, a Bruker handheld Tracer III-SD X-ray fluorescence analyzer uses a rhodium X-ray tube with a silicon drift detector that has a resolution of 145 kV (Figure 6) and a spot size of $\sim 0.5 \text{ cm}^2$. Spectra were acquired at a voltage of 40 kV, beam current of $6 \mu\text{A}$, and live time of 180 seconds. The depth of penetration was 4.61 cm (1.8 inches), passing through the entire stamp. Results were obtained by integrating the area under each peak and were grouped and averaged by issue. Twenty Chile

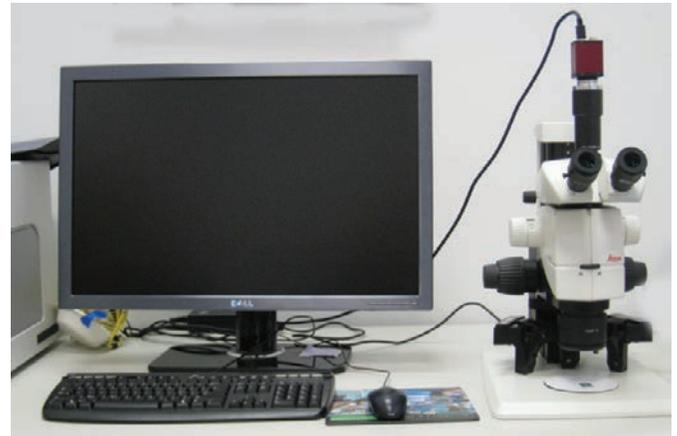


FIGURE 5. (top) Leica microscope and (bottom) Chile number 1 at $\times 100$ showing some bluing of the paper.

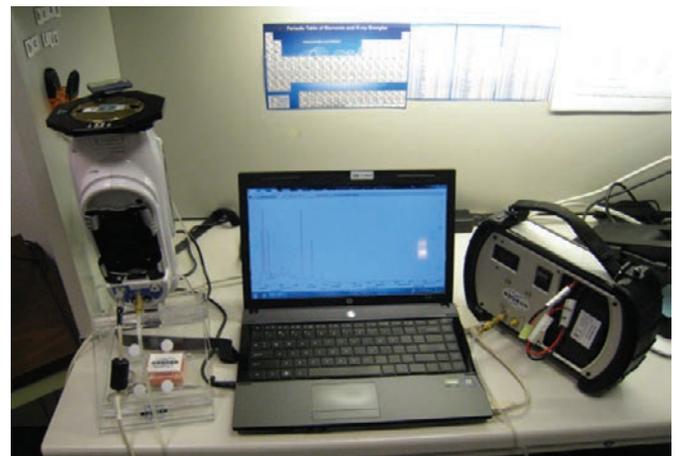


FIGURE 6. Bruker Tracer III-SD X-Ray Fluorescence Analyzer.

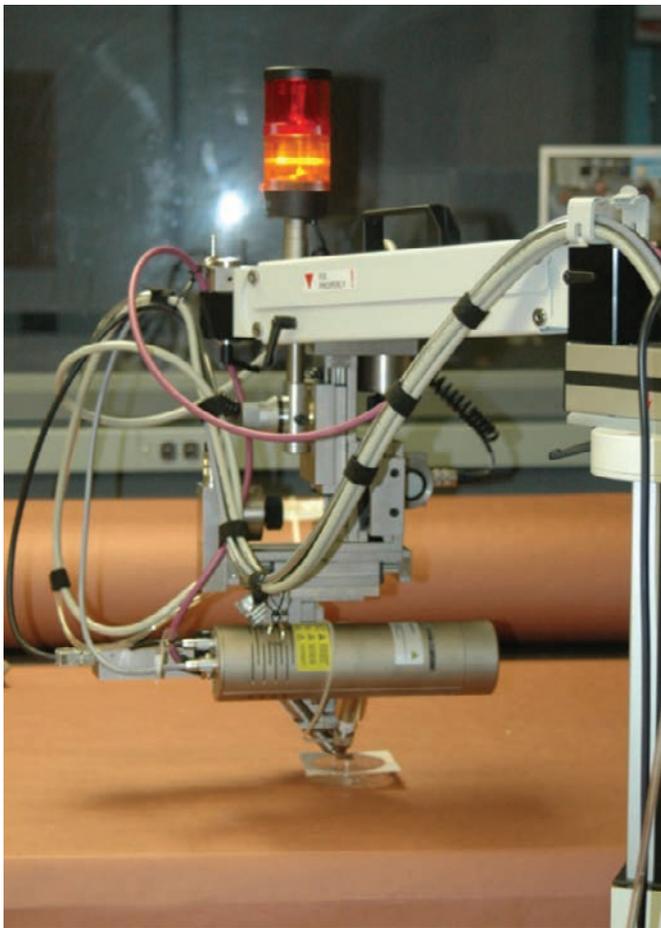


FIGURE 7. Bruker Artax XRF spectrometer.

number 1 stamps were averaged, as well as ten stamps for each of the other five London printings.

At MCI, a Bruker Artax X-ray fluorescence spectrometer with a rhodium X-ray tube, an 80 μm polycapillary lens, and a silicon drift detector (Figure 7) were used. Maps were acquired over the denomination indicator in the lower left corner at a resolution of 0.1 mm. Each spot was analyzed at 40 kV, 200 μA under helium atmosphere for a live time of 20 seconds. Using the Artax 7.2.5 software, all the spectra obtained in a map were summed, elements of interest were identified, and the concentrations for those elements were mapped. By looking at the maps produced for each element, it could quickly be observed whether an element was primarily in the ink, paper, or any cancellation or was a contaminant in the stamp.

FOURIER TRANSFORM INFRARED SPECTROSCOPY

Infrared analysis at the NPM was undertaken with the Bruker ALPHA FTIR Spectrometer (Figure 8) with a diamond



FIGURE 8. Bruker FTIR Alpha.

ATR sampling module. The spectrometer uses a deuterated triglycine sulfate (DTGS) detector. The data are collected over a spectral range of 4,000–650 cm^{-1} at 4 cm^{-1} spectral resolution for 24 scans. The depth of penetration varies with wavelength and for different materials; however, using a diamond ATR window, it can be estimated that the depth of penetration is approximately 2 μm .

Additional infrared spectroscopy was acquired at MCI using a diamond ATR GoldenGate accessory in a Thermo Nicolet 670 bench with a DTGS detector. Spectra were acquired at a resolution of 4 cm^{-1} for 64 scans. The recent acquisition of a diamond ATR objective for the Thermo Nicolet Continuum infrared microscope allowed microscopic infrared analysis of some stamps, and spectra were collected using this MCT/A detector between 4,000 and 650 cm^{-1} at a resolution of 4 cm^{-1} for 128 scans. (Figure 9).

X-RAY POWDER DIFFRACTION

The Rigaku D/Max Rapid (Figure 10) at MCI collimates monochromatic X-rays to a microbeam, which can be focused on samples as small as 100 micrometers in diameter. The instrument



FIGURE 9. Thermo Nicolet FT-IR with Continuum microscope.



FIGURE 10. Rigaku D/Max Rapid with stamps mounted for analysis.

moves the sample through an arc during X-ray exposure in order to randomize orientation of the crystallites with respect to the beam as much as possible. In this way, the characteristic angles of diffraction appear as whole or partial Debye cones. Patterns were collected using a copper X-ray tube using the K_{α} line. The

stamps were mounted on the holder using wax, with care taken to align the XRD sample spot so that the wax and aluminum holders were not in the area to be analyzed. Data were collected for five minutes using the 0.8 mm collimator while the goniometer was fixed at 0° (Φ) and 20° (Ω).

The XRD patterns produced, after background subtraction, were qualitatively matched using Jade 8.0 software to reference patterns of known materials in the International Center for Diffraction Data libraries and/or user libraries developed from reference materials. The depth of penetration into a sample is typically on the order of 20–100 μm , depending on the density and mass of elements, as well as the angle of incidence.

DATA ANALYSIS

MICROMETER RESULTS

Table 1 shows the thickness (in millimeters) of the six Chilean stamps following TAPPI T-411 standards, a method measuring single-sheet thickness and variations in single-sheet thickness of paper, tissue paper, and cardboard. No mint stamps were measured. The results from the micrometer were affected by surface roughness, cancellations, glue, and paper and hinge remnants.

CHROMATICITY RESULTS

The polygons drawn in Figure 11 represent the color gamut covered by all of the samples, constructed by determining the convex hull (CH) of the set of data points. The CH is the minimal convex set containing the data points. There are many different “colors” in the spectrometric sense, but only four in the perceptual sense. These results support the differentiations made between the two blue and the two red issues, given their clustering and overlaps. The visual determinations were made independently of the VSC 6000’s findings.

While color expert James Allen sorted and collated the shades of the Chilean stamps, a number of difficulties became apparent, including the underlying paper color or the bluing of the

TABLE 1. Micrometer results for 20 stamps.

Stamp	Thickness (mm)	Standard deviation (mm)
Chile 1 (red)	0.1161	0.0028
Chile 8 (red)	0.1227	0.0034
Chile 2 (blue)	0.1116	0.0085
Chile 12 (blue)	0.1349	0.0069
Chile 11 (yellow)	0.1411	0.0022
Chile 13 (green)	0.1098	0.0026

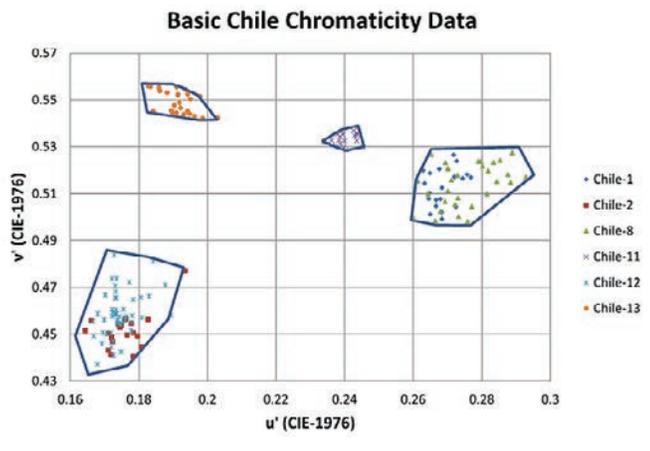


FIGURE 11. CIE 1976 u', v' chromaticity coordinates of the London printing of the Chile stamps.

paper affecting the color interpretation as a tint different (generally lighter) from that identified by the VSC 6000; the roughness of the stamp surface identified by oblique light reflections during data collection; and stamps that were either poorly inked or overinked, resulting in a certain level of “blotchiness.” Canceled and damaged stamps, paper differences, and other printing inconsistencies also contributed to the results, and all of the stamps had been soaked off cover and washed before affixing them to the album pages. As a rule, the stamp colors suffered from the cleaning process; for example, the 20 centavos became altered to a much lighter and sometimes a bluish green (Bacon, 1902).

The color expert applied de facto fuzzy membership functions and determined color ranges (Table 2), resulting in the identification of color variations that, while differentiable, are not that distinctive. They are likely the result of batch variations in ink or pigments, aging effects, and possible paper color transmission effects. When considering the size of the CHs relative to MacAdam ellipses, it is clear different color experts might well disagree on which shades fit which categories as the chromaticity moves away from the center of the individual CH.

The 5-centavos printings were probably a bright brick red color rather than the current brownish red. The reason for the various tints is the extenders used in the ink. The 10-centavos modified Prussian blue stamps were originally bright blue; however, after 150 years of aging, washing of the stamps, and environmental conditions, the color has changed to a deep or deeper bright blue.

An extender, also known as filler, in printing ink technology is a white transparent, or semitransparent, component whose purpose is to reduce the cost of the ink by increasing the area covered. It can reduce the color strength of the ink without adding any white color to it, which is useful if the pigment in the ink is very strong. Extenders can also be used to adjust the ink’s consistency and viscosity.

The most interesting stamp from the London printings is the 1-centavo stamp. There are several tints to this currently dullish green-yellow stamp. Because of the different amounts of lead chromate, aging 150 years and various environmental conditions darken and muddy the stamp colors. These stamps are considered changelings since they have dissolved to a “greenish” tint, while the original color was probably goldenrod. One surprising discovery seen under high magnification was the red spots found

TABLE 2. Colors and shades of the London printed Chile postage stamps identified by color expert.

Printing	5 centavos	10 centavos	1 centavo	20 centavos
First London printing, issued 1 July 1853	Brownish red with gradations of brightness on blued paper (Chile no. 1)	Prussian blue with gradations of deepness on yellowish-white paper (Chile no. 2)	–	–
Second London printing, issued May 1855	Brownish red with gradations of deepness on blued paper or cream-colored paper (Chile no. 8)	–	–	–
Third London printing, issued 1 January 1862	–	–	Olive yellow with shade variations of green and yellow on yellowish-white paper (Chile no. 11)	Dark green with gradations of deepness on yellowish-white paper (Chile no. 13)
Third London printing, issued October 1861	–	Deep blue with gradations of bright to deeper blue on yellowish white (Chile no. 12)	–	–

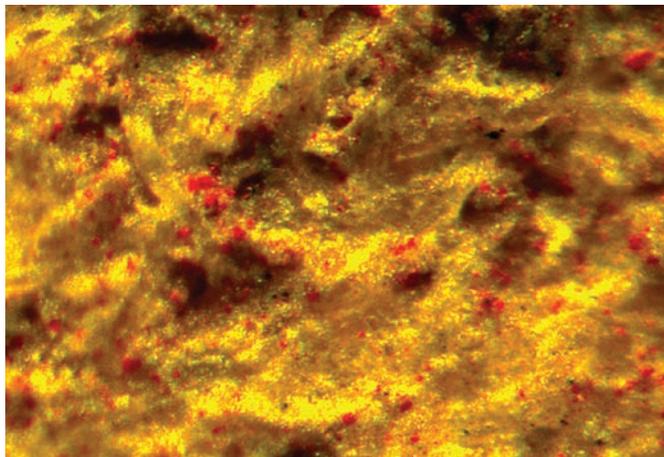


FIGURE 12. Chile number 11 showing the vermilion ink as red spots at $\times 1,600$.

in various quantities in every stamp (Figure 12). These spots are further discussed in later sections.

The 20-centavo stamp has two different tints: dark green and deeper green with the original color being a deep green.

It should be pointed out the VSC is a comparator and is not calibrated as an analytical instrument. Its results are indicative but not definite. As many colors are made by mixing pigments and organic dyes, the VSC cannot distinguish them, and its use for individual pigment identification may be restricted as seen in the limited amount of data in the infrared spectrum (Figure 13).

XRF RESULTS

The XRF spectra from the handheld portable XRF at the NPM and the accumulated Artax spectra from the XRF mapping data collected at MCI can be easily compared. The greater sensitivity of the Artax, using a helium flush in acquiring the elemental maps, allows detection of more fluorescence from the lower energy peaks from aluminum and silicon when compared to the Tracer data. This is reflected in the changes in element ratios, including aluminum and potassium, seen in Table 3.

However, overall, the data obtained from the two XRF methods are generally quite similar. The XRF maps are very useful in identifying any anomalies present. For example, the overall XRF spectrum from Chile number 2 (Figure 14) identifies a copper component in the ink, suggesting the use of an azurite colorant $[Cu_3(CO_3)_2(OH)_2]$. However, examination of the map shows the copper is a lone area of contamination (Figure 15) and not a component of the ink, so we can discount azurite as

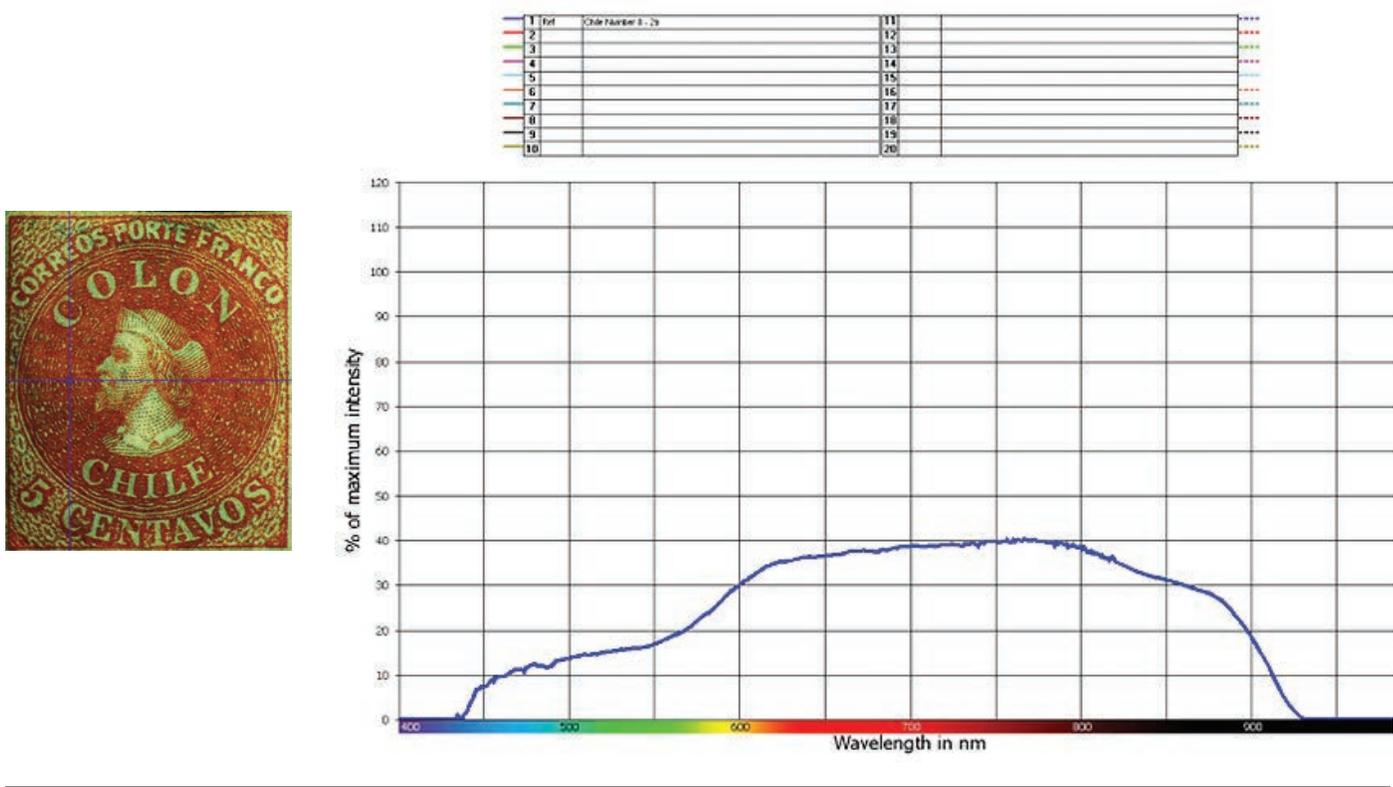


FIGURE 13. The reflectance curve of Chile number 8 showing no organic red dyes present.

TABLE 3. Element ratios of the London printed Chile postage stamps.

Stamp	Number averaged	Fe/K	K/Al	S/Al	S/K	Pb/Cr
Chile 1 (red)	20	9.11	5.75	8.91	1.55	–
Chile 1 (red)	2	8.22	5.32	12.72	2.62	–
Chile 8 (red)	10	9.04	5.50	9.66	1.76	–
Chile 8 (red)	2	11.63	3.93	9.76	3.35	–
Chile 2 (blue)	10	50.63	1.48	–	–	–
Chile 2 (blue)	1	30.60	3.14	–	–	–
Chile 12 (blue)	10	68.07	1.22	–	–	–
Chile 12 (blue)	3	32.97	7.75	–	–	–
Chile 11 (Yellow)	10	10.76	1.64	–	–	2.90
Chile 11 (Yellow)	2	4.70	10.09	–	–	2.71
Chile 13 (Green)	10	95.18	0.55	–	–	5.13
Chile 13 (Green)	2	18.16	3.03	–	–	4.20

a possible ink component. The data clearly show that both lead (Pb) and iron (Fe) are components of the ink.

The 5-centavo stamps (Figure 16) show major amounts of calcium and iron. The inclusion of trace levels of manganese in addition to major iron peaks suggests the use of an iron oxide earth, for example, the nineteenth century Venice red (Fe_2O_3), as the primary inorganic red colorant. However, the use of red lead (Pb_3O_4) or organic red colorants cannot be eliminated. In

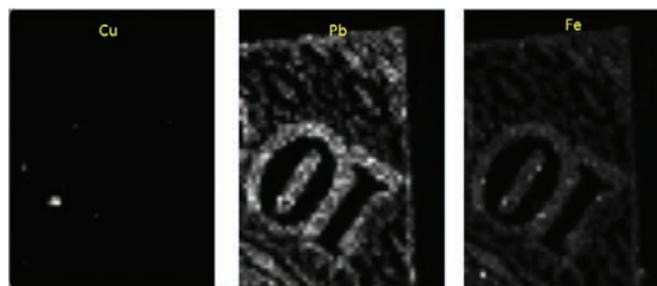


FIGURE 15. XRF map from Chile number 2.

addition, Prussian red, $\text{K}_3[\text{Fe}^{\text{III}}(\text{CN})_6]$, is known to be used by Perkins and Bacon and is suggested by the identification of minor levels of potassium in the ink.

The 10-centavo stamps as seen in Figure 14 show major amounts of lead and minor amounts of iron and calcium. The large amount of lead and iron in a blue stamp suggests the use of lead white ($\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) with a Prussian blue colorant. It should be noted that the large amount of lead present in the 10-centavo stamps makes it difficult to determine if sulfur is present due to the overlap of the sulfur K peak with the lead Pb M peaks at 2.3 keV.

The 1- and 10-centavo stamps both show lead, sulfur, and chromate, suggesting the use of a lead chromate yellow. The mercury identified in the yellow ink suggests an identification of the red spots (Figure 12) visible under the microscope as vermilion

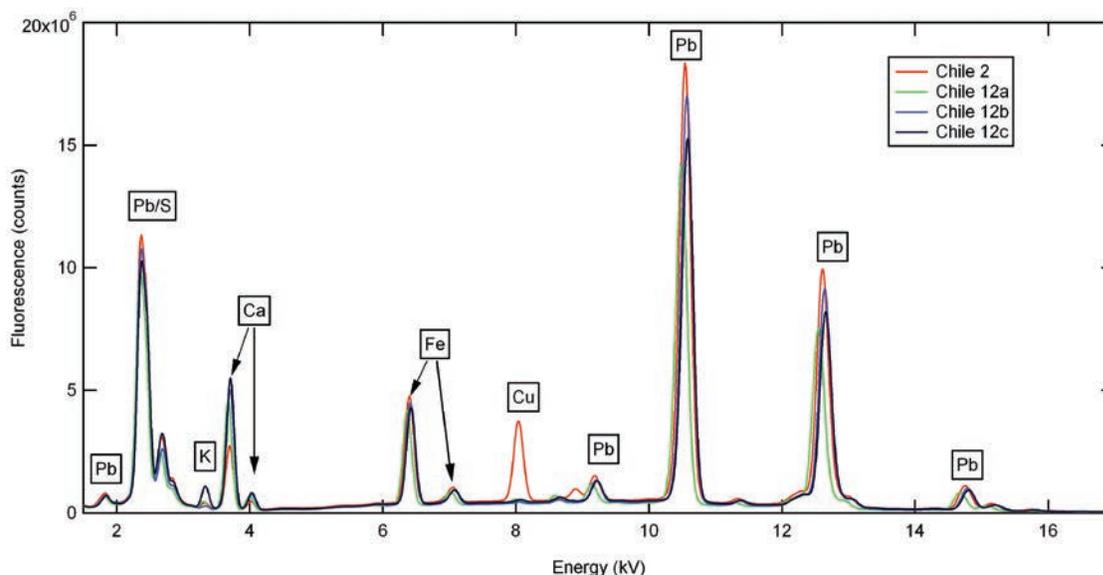


FIGURE 14. Accumulated XRF spectra of blue stamp maps by Perkins, Bacon & Co., 1853 (Chile number 2) and 1861/2 (Chile numbers 12a, 12b, and 12c).

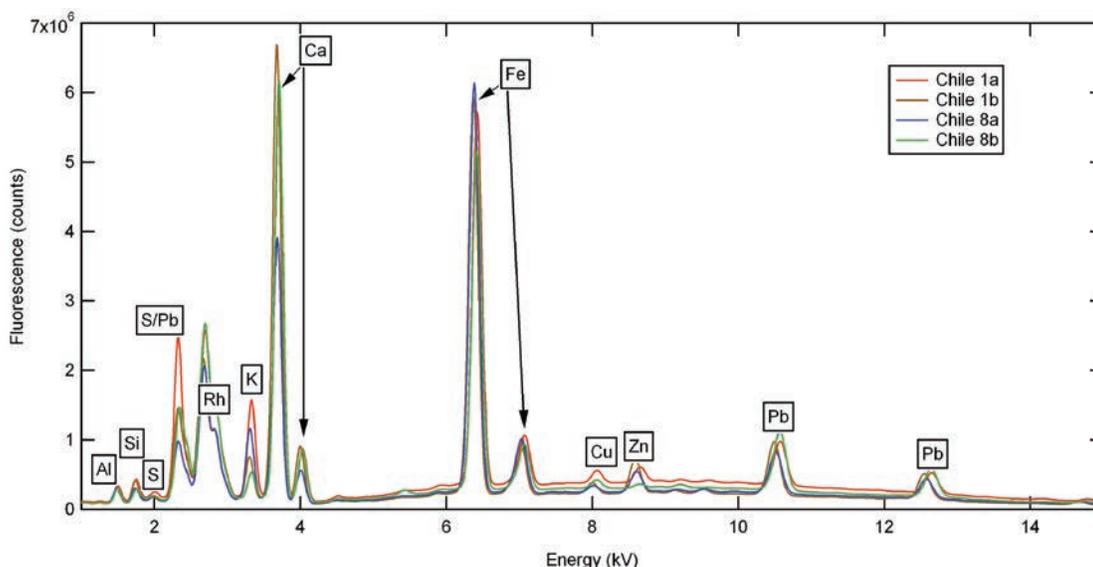


FIGURE 16. Accumulated XRF spectra of red stamp maps from Perkins, Bacon & Co., 1853 (Chile numbers 1a and 1b) and 1855 (Chile numbers 8a and 8b).

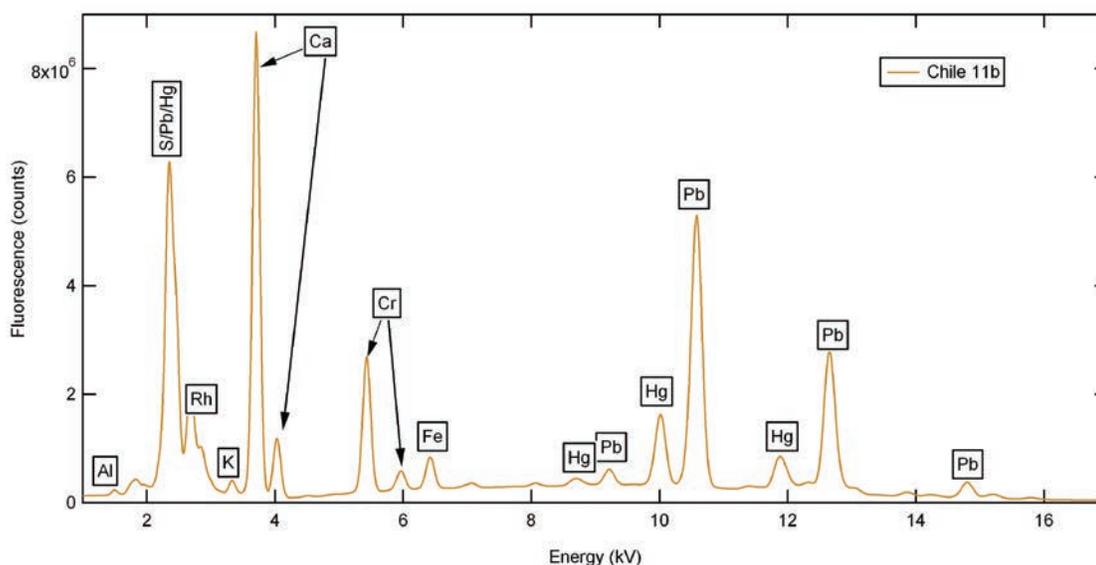


FIGURE 17. Sample of XRF results for Chile number 11.

or cinnabar (HgS). Figure 17 shows the results for the 1-centavo stamps (Chile number 11).

Infrared spectroscopy shows that the large calcium peak present in the yellow and blue inks is from a calcium carbonate filler in the inks. It is interesting to note the green ink used in the 20-centavo stamp contains only minor amounts of calcium, while significant amounts of calcium are present in the yellow

ink. The peaks from potassium, sulfur, and aluminum present to varying amounts in all the stamps are likely from the use of alum KAlSO_4 .

The analysis of the six London printed stamps of Chile showed several interesting ratios of elements. The lead/chrome ratios in the yellow and green inks differ slightly; the yellow ink has a higher amount of lead to chrome than the green ink. The ratios

for the Chile 1 and 8 issues and the 2 and 12 issues are similar and do not show any significant differences between the two printings.

FTIR RESULTS

In all the IR spectra there is a large contribution from the paper on which the stamps were printed. In cases where no gum or adhesive remained on the back of the stamp, a reference spectrum of the paper could be easily compared to the infrared spectrum of an inked area to identify the contributions of the paper (Figure 18). Infrared spectroscopy was able to identify a number of white pigments that were added to the inks. In all stamps calcite (CaCO_3), also referred to as chalk or whiting, has been identified. In the red ink, calcite appears to be the only white pigment present, whereas in the blue inks, lead white (hydrocerussite) was used primarily, with small amounts of calcite also present.

The cyanide bands present in the red inks vary in different stamps and in different locations within the same stamp. Peaks at 2,080, 2,060, and 2,040 cm^{-1} have all been identified, with the main peaks occurring at 2,080 and 2,060 cm^{-1} . This is in agreement with the results found in the penny red stamps examined by Ferrer and Vila (2006). The peak around 2,080 cm^{-1} can also be seen in the blue and green inks, here from Prussian blue originally present in the inks. Unfortunately, the cyanide bands occurring in the 2,040–2,090 cm^{-1} region are not distinct enough to identify specific ferrocyanide and ferricyanide components. For example, both soluble and insoluble forms of Prussian blue, $\text{Fe}_4^{\text{III}}[\text{Fe}_2^{\text{II}}(\text{CN})_6]$ and $\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$ and $\text{KFe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$, are said to absorb at 2,080 cm^{-1} (Berrie, 1997). It is likely that additional work in this area may be able to further elucidate the initial ink components.

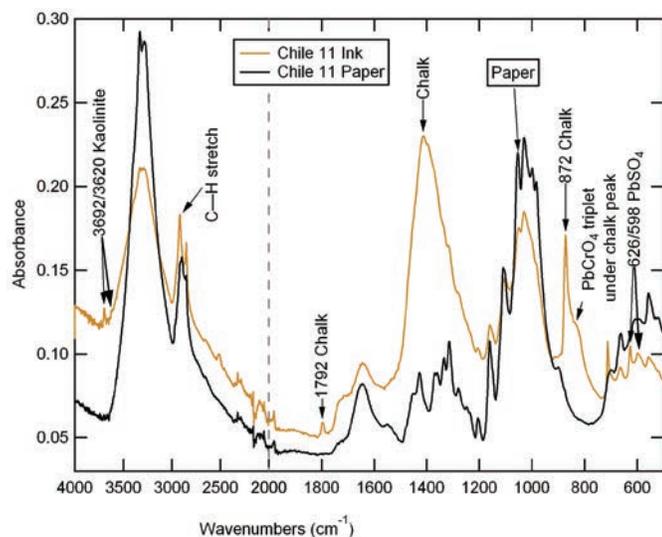


FIGURE 18. Infrared spectra from front and reverse of Chile number 11 showing contributions of paper and ink.

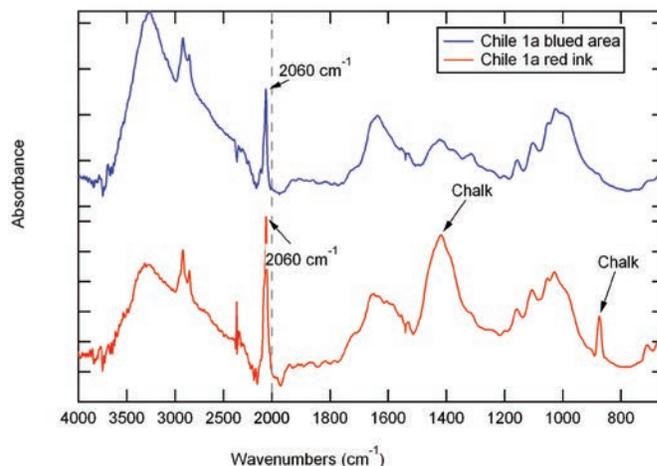


FIGURE 19. The μ ATR-FTIR of blued ink on 1853 Perkins and Bacon red stamp (Chile number 1a).

In the yellow and green inks, peaks from the colorants could be clearly identified in the infrared spectra. Peaks characteristic of lead sulfate appear in the yellow ink, in addition to large peaks from calcite. The green ink contains a significantly smaller amount of chalk than the yellow ink, which allows the lead chromate peaks centered around 850 cm^{-1} to be identified.

The ATR objective on the microscope could not be used on all of the stamps in the study, but use on the Chile 1 issue allowed tracking of the cyanide components of the red ink into the blued areas (see Figures 5 and 19). Although the blued areas show none of the chalk component of the ink, a cyanide band at 2,060 cm^{-1} is still present.

Although both linseed oil and beeswax are known to be components of the ink, most of the characteristic bands for these media are hidden under the absorption peaks from the paper or other ink components. The strong bands in the C–H stretch region, at approximately 2,890 and 2,850 cm^{-1} , are present due to the hydrocarbon chains in both linseed oil and beeswax. When comparing the ink spectra to the paper spectra both obtained from all the stamps, a broad shoulder at approximately 1,730 cm^{-1} is present. This can be attributed to the carbonyl groups present in both vegetable oils and beeswax. However, neither the carbonyl nor the C–H stretch absorption should be considered definitive proof of a vegetable oil/beeswax binder. Both calcium and lead fatty acid soaps, which are formed when the ink components interacted with the linseed oil and stearates in the beeswax, were identified in the blue inks.

XRD RESULTS

Using an 800 μm diameter collimator, X-ray diffraction confirmed the identification of lead chromate (PbCrO_4) in the yellow and green inks; in addition, it was able to confirm the

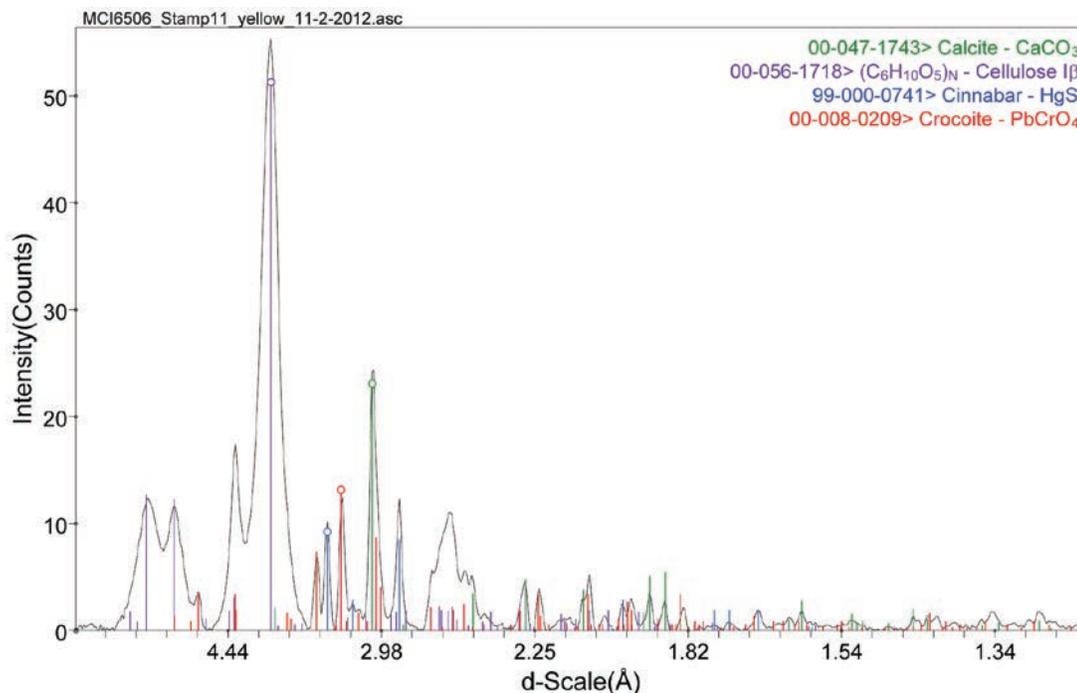


FIGURE 20. XRD data from yellow ink area of Chile number 11 stamp.

identification of the red spots in the yellow ink as vermilion (Figure 20). As in the FTIR, calcite was identified in all four inks. Crystalline fatty acid soaps were identified in the red ink. XRD of the paper areas of the stamps examined only identified cellulose of varying degrees of crystallinity.

DISCUSSION AND CONCLUSIONS

Nondestructive analysis of the stamps was completed using instruments at the Smithsonian National Postal Museum and the Smithsonian Museum Conservation Institute. A large-scale analysis (10–100 mm²) provides overall examination of ink and paper simultaneously, while small-scale analysis (0.01–0.1 mm²) allows a better discrimination between paper and ink data.

While all the techniques employed have limitations when used individually, complementary use of the techniques and comparison of the data allow for better understanding of the results obtained by an individual instrument as well as a more thorough characterization of the stamps (Table 4). Although the specific presence of beeswax or linseed oil cannot be determined, the identification of fatty acid soaps in the XRD and IR data, as well as the strong C–H stretch bands in the IR data, indicate a vegetable oil or beeswax-based binding medium was likely used.

Whiting (calcite) was identified in all of the inks examined, while lead white was used additionally in the blue inks. This is

likely due to the high tinting strength of Prussian blue, which requires only a small amount of the pigment to produce a deep blue color. When Prussian blue was used in the green ink, it was not accompanied by lead white. The yellow pigment used in both the yellow and green inks is a chrome yellow (PbCrO₄). A further support for the likely original goldenrod tint of the yellow stamps, rather than the current muddy green-yellow tint, is the inclusion of a small amount of the red vermilion pigment in the yellow ink.

Vermilion was not identified in the red inks used. The presence of manganese in the XRF spectra of the red stamps and the presence of kaolinite (Al₂Si₂O₅(OH)₄) in the IR spectra of the red inks suggest at least some of the red color is due to the inclusion of a red iron oxide (Fe₂O₃). Unfortunately, the generally non-crystalline nature of earth pigments meant no confirmation of this could be found using XRD. Although Ferrar and Vila found gypsum used in the penny red stamps also printed by Perkins and Bacon (Ferrar and Vila, 2006), no gypsum was identified in either the IR or XRD data.

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TABLE 4. Characterization of the London printed Chile postage stamps.

Stamp number	Color	Year of issue	FTIR results	XRF results	XRD results
1	Red	1853	Calcite (1400, 872); kaolinite (3600, 3695); cyanide peaks (2060, 2080)	Major: Fe, Ca; Minor/trace: Pb, K, S, P, Al	Calcite; fatty acid soaps
2	Blue	1853	Lead white (br 1400 678); Prussian blue (2088); fatty acid soaps (1540, 1510); traces of calcite (872)	Major: Pb, Fe; Minor/trace: Ca, Al, K; Sulfur undetermined	Hydrocerussite; cerussite; calcite
8	Red	1855	Calcite (1400, 872); kaolinite (3600, 3695); cyanide peaks (2060, 2080)	Major: Fe, Ca; Minor/trace: Pb, K, S, P, Al	Calcite
11	Yellow	1862	Calcite (1400, 872); lead sulfate (627, 596)	Major: Ca, Pb; Minor/trace: S, Cr, Hg, Fe, K, Al	Lead chromate; vermilion; calcite
12	Blue	1861	Lead white (br 1400 678); Prussian blue (2088); fatty acid soaps (1540, 1510); traces of calcite (872)	Major: Pb, Fe; Minor/trace: Ca, Al, K; Sulfur undetermined	Hydrocerussite; cerussite; calcite
13	Green	1862	Lead sulfate (627, 596); lead chromate (850 trace); Prussian blue (2086); trace calcite (872)	Major: Pb, S; Minor/trace: Cr, Fe, Ca, K, Al	Lead chromate; possible calcite; possible minium or red lead

which contained information on Lewis Berger & Sons, an ink supplier to Perkins, Bacon & Co. James Allen identified the various shades and colors of the stamps, and Harry Brittain verified our FTIR and XRD results using the equipment in his laboratory.

NOTES

1. Scott numbers are from *1998 Standard Postage Stamp Catalogue—Volume 2 (Countries C–F)*. The third printing had two different dates of issue: October 1861 for the 10¢ and January 1862 for the 1¢ and 20¢.

2. Most commonly, the powder diffraction file produced by the International Centre Diffraction Data, Newtown Square, Pa., <http://www.icdd.com> (accessed 15 January 2013).

3. The Bernard Peyton Specialized Collection of Chile (accession number 223486), which was donated to the Smithsonian National Philatelic Collection on 23 December 1958, consists of two albums and is a comprehensive study of the different color shades of the first issues of Chile from 1853–1967.

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