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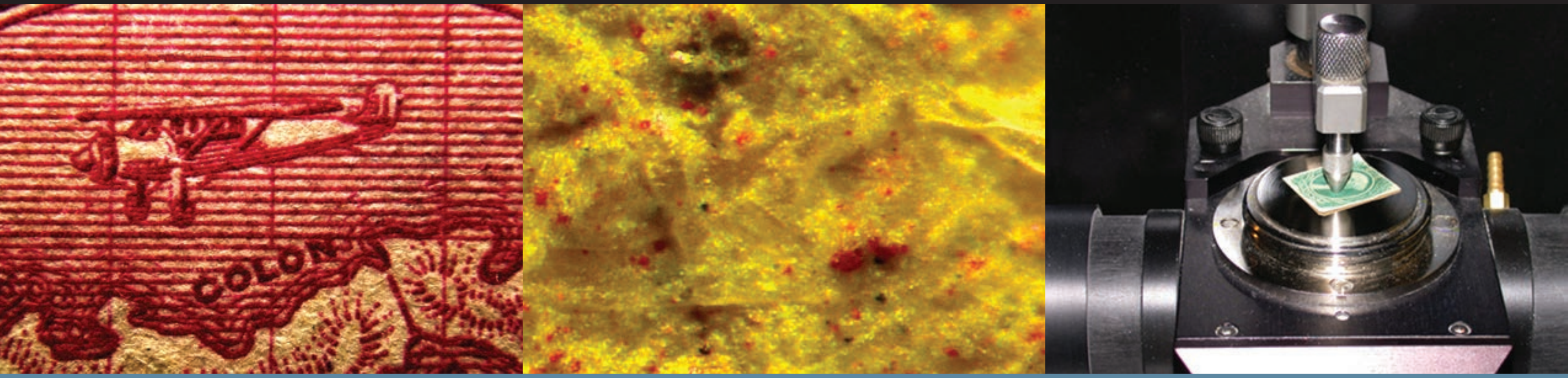

Proceedings of the First International Symposium on Analytical Methods in Philately

Edited by
Thomas Lera, John H. Barwis,
and David L. Herendeen

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ABSTRACT

Lera, Thomas, John H. Barwis, and David L. Herendeen. Proceedings of the First International Symposium on Analytical Methods in Philately. *Smithsonian Contributions to History and Technology,* number 57, x + 122 pages, 111 figures, 22 tables, 2013.—This publication contains papers presented at the First International Symposium on Analytical Methods in Philately, hosted by the National Postal Museum in November 2012. Readers will find insights to research methods used across the entire spectrum of philatelic interests, from composition and physical characteristics of paper, to the chemistry and mineralogy of printing ink, to determining the genuineness of stamps, overprints, and the uses of adhesives on cover. Some of these projects were funded in part by the Institute for Analytical Philately and the National Postal Museum.

Cover images, from left to right: Detail of 1941 Republic of Panama Air Mail Stamp (Scott C6B); Figure 12 of "A Scientific Analysis of the First Issues of Chile 1853–1862;" and Figure 3 of "Infrared Spectroscopic and X-Ray Diffraction Studies of the Typographed Confederate 5¢ Stamps."

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ABSTRACTS

Welcome Letter

June 1, 2013

It is my great pleasure to present the *Proceedings of the First International Symposium on Analytical Methods in Philately*. The Smithsonian National Postal Museum (NPM) hosted this premier meeting on 12–14 November 2012 in the Winton M. Blount Center for Postal Studies.

This international symposium was, to our knowledge, the first ever held. It offered an opportunity for interested philatelists and scientists to get together, share their methodologies, highlight new technologies, and provide long-term, wide-ranging benefits to all aspects of philately and helped set the course for future forensic analyses in the philatelic arena. Our close working relationship with the Institute for Analytical Philately, Inc. was a huge plus because the NPM allowed philatelists to use state-of-the-art equipment for their advanced research efforts.

The success of the symposium was due in large part to David Herendeen, president and founder of the Institute for Analytic Philately, Inc., and Thomas Lera, NPM Winton M. Blount Research Chair, as well as the speakers, the demonstrations, and the more than 50 attendees. Special thanks go to Elizabeth Simmonds, NPM event coordinator. Without her efforts, the symposium would not have been as great of a success.

If you enjoy these papers as much as I hope you will, please continue to support the National Postal Museum, the Institute for Analytical Philately, Inc., and future symposiums.

Allan Kane
Director, National Postal Museum

Preface

The Institute for Analytical Philately, Inc. (IAP) was formed in 2010 as a philanthropic, nonprofit corporation dedicated to deepening the understanding of philatelic materials through the use of scientific technology and publication of experimental results. The support IAP provides can be tailored to the needs of any philatelist, from those with no scientific background to those with advanced degrees in science or engineering.

IAP grants typically range from $2,000 to $4,000 and are intended to help fund travel, lodging, and laboratory use. Additional funding may be available through cost sharing with alliance members, who can also provide advice on previous work done in a particular area or help in conceiving and planning a research effort. Current alliance partners include the Smithsonian National Postal Museum (NPM), the U.S. Philatelic Classics Society, Inc., the Confederate Stamp Alliance, the Vincent G. Greene Philatelic Research Foundation (Canada), and the Philatelic Foundation. Detailed information on grants and NPM scholarships can be found on page 115.

Researchers may conduct their work anywhere they choose but are encouraged to take advantage of the facilities and expertise available at IAP's centers of excellence, where they will find state-of-the-art equipment and experienced advisors like at the Smithsonian National Postal Museum, where a broad range of equipment and expert guidance is available.

This book contains papers presented at the First International Symposium on Analytical Methods in Philately, hosted by the National Postal Museum in November 2012. Readers will find insights to research methods used across the entire spectrum of philatelic interests, from the composition and physical characteristics of paper to the chemistry and mineralogy of printing ink to determining the genuineness of stamps and overprints, and to the uses of adhesives on cover. Some of these projects were funded in part by IAP and NPM. Some of the presenters have already had their research published, so for those presentations we have included abstracts and citations.

The symposium also included one day of hands-on training and demonstrations using equipment from the NPM research lab led by manufacturers' representatives.

We plan to host another international symposium, the timing of which will depend on the pace and volume of research conducted over the next one to two years. In the meantime, we encourage you to get involved in investigating philatelic mysteries. For more information about IAP visit www.analyticalphilately.org, and for information on the NPM visit www.postalmuseum.si.edu.

Dr. John H. Barwis, FRPSL
Institute for Analytical Philately,
President

Thomas Lera, FRPSL
Smithsonian National Postal Museum,
Research Chair

David L. Herendeen, 1946–2013

David L. Herendeen, founder and first president of the Institute for Analytical Philately, died suddenly on 4 January 2013 in Las Vegas. David was a stamp collector since childhood and specialized in worldwide postage-due stamps and postal history for more than 35 years. His exhibits of British Empire and French community postage-dues won many national gold medals, grand awards, and two international gold medals. He held many positions in organized philately, including president of the France and Colonies Philatelic Society (2004–2007), first vice president and board member of the American Philatelic Congress (1997–2010), and vice president (2003–2006) and board member of the American Association of Philatelic Exhibitors (2000–2010). He was both a nationally accredited and a chief judge, serving in these capacities for more than 15 years. He was also an active writer and published major research articles in many publications, including *The London Philatelist, The Collectors Club Philatelist*, and *The Congress Books*. Additionally, he was an editor of the *France and Colonies Philatelist* (2007–2013) and the *British Caribbean Philatelic Journal* (1997–1999). His book *The Parcel Post Stamps of the Ivory Coast* received a gold medal at Stampshow 2001.

David retired as a senior executive of an engineering and software consulting company after a 35-year career performing and managing government-related research and development activities. He held a degree in mathematics and computer science from the University of California, Los Angeles (UCLA) and took numerous graduate and career development courses at the State University of New York, UCLA, and the California Institute of Technology.

David's interest and experience in engineering and mathematics expressed themselves in his philatelic studies and ultimately led to his suggesting the idea for the IAP to a small group of like-minded colleagues. His belief that analytical methods held wide interest among philatelists was quickly validated when nearly 100 people joined the new organization within a year of its launch. We are committed to continuing his work.

David was a man of conviction, honor, and principles. He was passionate about knowledge and was inquisitive about much of what makes our life as stamp collectors worth living. He will be missed by all who knew him and who shared his laughter and joy of philatelic pursuits.

John H. Barwis
Thomas Lera

Keynote Address: The Place for New Tools in Forensic Philately

David R. Beech

INTRODUCTION

This paper relates to my realization, reinforced by my access to the developments at the British Library for the conservation and preservation of rare documents, that certain philatelic problems could be better solved or understood by the quantitative methods traditionally associated with the physical sciences than by the taxonomical methods traditionally associated with the biological sciences. In 2001, I worked with University College London on a project to use spectrographic analysis to study the very rare (and valuable) "Post Office" Mauritius stamps of 1847, developing definitive information about the inks used and establishing a basis for a similar study in 2002 that evaluated the 1851–1852 so-called Grinnell Missionary stamps of Hawaii.

My views and observations on the expertization in conjunction with the recent development of advanced methods (some of which will be discussed in detail in the papers presented) for performing various analyses on postage stamps and other postal matter are largely based on supporting the Expert Committee of the Royal Philatelic Society London. It should be noted that it is not the purview of the Institute for Analytical Philately, Inc., the Smithsonian National Postal Museum, or the British Library to provide expertization services.

A NEW BEGINNING

It is almost impossible to overestimate the importance of the First International Symposium on Analytical Methods in Philately held in November 2012 at the Smithsonian National Postal Museum, Washington, D.C. This event was organized by the Institute for Analytical Philately, Inc. As the institute is comparatively new, having been established in 2009, its first public meeting is a key opportunity to establish its credentials along with a number of principles that will set the scene for the future.

I am pleased to have had the opportunity to present the keynote address, and I intend to touch on several important aspects of analytical philately and its application to expertization. While a taxonomical analysis, associated with the "English school" of philately, may easily afford the detection of "bogus" issues, quantitative analysis for the detection of forgeries, associated with the "French school," has long been hampered by the cost and availability of appropriate technologies. But, to a certain extent, that is no longer the case because over the last decade the availability and ease of use of nondestructive analytical equipment has grown while its cost has decreased dramatically. Some

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of this equipment is now within the grasp of major museums and expertizing bodies and can be used to disclose sophisticated forgeries.

In the earliest days of philately, the English school emphasized the postage stamp design, ignoring differences in paper, shade, perforation, watermark, etc. The French school required some close study and some tools, beginning with the magnifying glass. Later came accurate measurement, perforation gauges, and watermark fluid. More high tech methods occurred when ultraviolet light was deployed to detect alterations or the removal of postal markings. During the 1960s, Cheavin (1885–1968) used X-rays to detect altered stamps (Cheavin, 1950). In recent years it has been suggested that he was also making the altered stamps about which he wrote.

My involvement with more advanced analytical methods dates from 2001 when the British Library started working with Professor Clark and his student colleagues at University College London (Clark, 1999). They were examining pigments on manuscripts and early printed books, maps, and other paper artifacts by Raman spectroscopy.

One project was to look at the inks on Mauritius 1847 1d and 2d "Post Office" issue (see Figure 1 for one of the five known covers with the 1d stamp) and of the 1858–1862 Britannia issue using examples in the Tapling Collection.[1] We were able to determine the pigments involved (Chaplin et al., 2004) and thus established a standard against which others can be judged (and have been judged, for the 1847 issue) by the Expert Committee of the Royal Philatelic Society London.

During 2002 I became involved in the question of the expertization of the Hawaii 1851–1852 Grinnell Missionary stamps. Earlier examinations had proved inconclusive (Chaplin et al., 2002), but, using Raman spectroscopy to compare the stamps in the Tapling Collection, known by their provenance to be genuine (Figure 2), with the Grinnell examples that were the property of the Shattuck family, the Expert Committee of the Royal Philatelic Society London determined that the Grinnells were forgeries (Pearson, 2006).

I have since been involved in other Raman work with Professor Clark, and in due course a paper about aspects of the Chalon issues of New Zealand will appear.

Analytical philately is the use of chemical, physical, mathematical, or other quantitative scientific methods to establish the facts in any philatelic matter. The facts, or evidence, are examined, with the end result of establishing the truth about a theory, the color, or the genuineness of a philatelic item. This may not be so easy.

The expertization of philatelic material has always been of the first importance. Publications on the detection of forgeries began to appear in the 1860s. Expertization took an organizational advance when in 1894 the Philatelic Society, London—now the Royal Philatelic Society London—formed the first expert committee. I have come to see such committees as "the

FIGURE 1. The Post Office Mauritius issue of 1847 (the Tapling Collection, Courtesy British Library).

FIGURE 2. The Hawaiian Missionary stamps of 1851 (the Tapling Collection, Courtesy British Library).

courts of law" in philately, and, while they only give opinions, they represent the best we have in establishing the truth.

If committees or expertizers are the philatelic courts of law, what standard of proof is required for a clear verdict? Does science offer absolute proof? Can an argument of probabilities prove sufficient? What are the possibilities of misinterpretation? Perhaps this symposium will help to answer some of these questions.

Philatelic expertization is probably at something of a crossroads as new technologies have become available for the application of scientific methods. The identification of shades, a longtime problem, might be much improved. (I think that the visual discrimination of shades of color is insufficient without an analysis of the pigments and their prospects for change.) With the need of expertizers to embrace scientific analysis, will single experts, common in continental Europe, still be able to function with what might be the new standards of evidence? I have suggested in a paper (Beech, 2008) that perhaps in the near future an expert certificate should be

- an opinion as to genuineness;
- a record of its provenance (for sufficient rarities); and
- a record of any treatments used in conservation, with a full photographic record and a record of any special scientific analyses, such as examinations by colorimetric methods and Raman spectroscopy.

If items submitted for opinion need any subsequent scientific analysis, who will do the work and how will it be paid for? How will those who run expertizing organizations be confident of scientific advice? As with the expertization of the Hawaii 1851–1852 Grinnell stamps by the Expert Committee of the Royal Philatelic Society London in 2006, some text in addition to a certificate simply stating "genuine" or "forgery" will be required. It must provide the evidence and technical details, if only for such scientific work to be repeated independently.

CONCLUSIONS

Much opinion today is based on evidence of earlier technologies, which the author's Grinnell work showed were not sufficient to distinguish the status of the Tapling and Grinnell Hawaiian Missionaries. The challenge to expertizers is to have a good understanding of the new techniques of science. The philatelic expertizer must have a good understanding of taxonomical and quantitative methods and the philatelic background of the items under consideration. But how is experience to be balanced with science? It seems clear scientific methods have much to offer, with this symposium being a clear learning ground, but we must use judgment in arriving at our final determinations.

NOTE

1. The Tapling Collection was formed by the wealthy Victorian businessman Thomas Keay Tapling, MP. It was bequeathed on his early death at the age of 35 in 1891. The collection is unrivalled in that it is the only major one formed during the nineteenth century that is still intact and contains almost all issues of postage stamps and postal stationery as well as most of the rarities issued up to 1890;

see http://www.bl.uk/reshelp/findhelprestype/philatelic/philateliccollections/articles/articletapling/articlestapling.html (accessed 1 November 2012).

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Paper Characteristics of U.S. 3¢ Stamps, 1870–1881

John H. Barwis

ABSTRACT. This paper describes laboratory research conducted on the United States 3¢ issues of 1870, 1873, 1879, and 1881 (Scott catalog numbers 147, 158, 184, and 207, respectively) to characterize the types of paper used by the three private printing companies that produced these stamps. The goal of this work was to quantitatively determine how many different papers each company used and which of these papers may have been used by more than one company. Analyses included measurement of paper thickness, fiber length and deformation, bending resistance, permeability, and sizing chemistry. The results demonstrate that combinations of these variables discriminate between the multiple paper types used by each company. The results of this research show that the banknote company issues comprise a more extensive range of paper types than have been assumed by collectors over the past 100 years. Thickness frequency distribution data are shown to provide important clues about whether thickness variations are simply normal artifacts of manufacturing or whether they represent multiple paper types with different mean thicknesses. Results also provide insight to papermaking practices of the 1870s and 1880s, with particular regard to composition, quality control of thickness, and the use of sizing to improve paper quality.

HISTORICAL BACKGROUND

Prior to 1894 all United States postage stamps were manufactured under contracts with private printing companies. Stamps manufactured between 1870 and 1889, the so-called "large banknote issues," were produced by three corporations originally involved in printing currency and security paper: the National, Continental, and American Bank Note Companies. From 1870 through 1882, these companies printed more than 21.2 billion stamps in twelve values, using papers that varied in both thickness and texture. Historical information about these papers is unavailable, as the government printing contracts provided no technical details on the materials to be used. No information has been found about the paper mills that supplied the printing contractors or about the products they provided.

The four printings of these issues are relatively easy to identify. Small design details differentiate National and Continental stamps as well as the two American printings (Figure 1). In late 1878, a so-called "soft" paper used by Continental is likely to have remained in use after Continental was acquired by American in February 1879. Proof of a Continental Bank Note Company origin of those stamps therefore depends on covers dated prior to American's takeover.

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FIGURE 1. The four printings discussed in this paper. Shades vary widely, and most are not diagnostic as to printing. Stamp scans courtesy of Robert A. Siegel Auction Galleries, Inc.

Collectors have been aware of banknote issue paper variations for more than 100 years and have characterized them using a wide range of qualitative descriptions, as summarized in Table 1. For most collectors it is sufficient to say the National and Continental papers tend to be thinner, stiffer, and more translucent than the thicker and softer American papers, and the sound from a “snap test” helps identify the two general groups. Controversies nevertheless remain among specialists:

- How many papers were used by these companies, and what characterizes them?
- Did the National and Continental Bank Note Companies use the same paper?
- Is the paper used by Continental in late 1878 the same paper first used by American?

DATA COLLECTION

From an unsorted group of used, off-cover 3¢ greens, stamps were first allocated to their appropriate printing. Fifty of the most poorly centered stamps were chosen from each printing to ensure at least one wide margin for measuring thickness on noninked areas. Each stamp was numbered so that data collected could be linked to unique samples. The intent was to facilitate comparisons of parameters other than thickness, should distinct thickness-based subpopulations be established within a given printing.

Paper thicknesses were measured by the author. Fiber composition was determined by Robert Hisey, a professional paper engineer. Tests for sizing composition were conducted at Hope College’s Department of Chemistry. All other measurements and their analyses were done at the Center for Ink and Printability in the College of Engineering and Applied Sciences at Western Michigan University (Pekarovic et al., 2011; Pekarovicova et al., 2012).

Paper Thickness

The thickness of each stamp was determined by averaging three measurements of an ink-free margin. A Mitutoyo handheld micrometer with an anvil diameter of 0.25 inch (~6.4 mm) was used, which allowed each measurement to represent an area of at least 6 mm^2. This approach was preferred to caliper-based point measurements, which may overrepresent small-scale surface irregularities. The micrometer’s precision is 0.001 inch (0.0025 mm), and the digital display makes it easy to interpolate to the next decimal place.

The printed area of every stamp was also measured to test thickness of the ink layer. Results varied widely enough

TABLE 1. Principal paper types of the large banknote issues as seen by various observers.

Author	National BN Co. 1870 issue	Continental BN Co. 1873 issue	American BN Co. 1879 issue	American BN Co. 1881 issue
Luff (1902)	White wove, thin to moderately thick	1. Stiff, hard, thin to thick 2. Semitransparent, almost pelure 3. Porous but thinner than type 4 4. Thick, soft, porous	Soft, porous, same as 1873 type 4	Same as 1879
Wiley (1915)	Hard, average thickness 0.00275 inches	1. Hard, average thickness 0.00275 inches 2. Soft "American" paper	Soft, average thickness 0.00330 inches	Soft, average thickness 0.00330 inches
Brookman (1966)	1. Hard, white, smooth surfaced, thin 2. A little thicker, slightly less hard than normal	1. Hard, same as National type 1 2. Soft "American" paper	1. Very soft, coarse mesh, more yellowish and not as smooth as hard papers 2. Intermediate paper, same stiffness as hard paper but more opaque	Very soft
Landau (1999, 2000)	Thin, hard, white, starch sizing	Thin, hard, white, starch sizing	Unbleached newsprint, soft, straw to ivory color	Unbleached newsprint, soft, straw to ivory color
Barwis (2001)	n/a	1. Thin, hard, close wove 2. Thin, hard, open wove 3. Medium, soft, open wove 4. Thick, soft, open wove	n/a	n/a
Scott Publishing Co. (2012)	White wove, thin to medium thick	White wove, thin to thick	Soft, porous	Soft, porous

(0.0002–0.0009 inch) to demonstrate that measurements of inked areas would not yield an accurate assessment of paper thickness.

BENDING RESISTANCE

The bending resistance of 50 stamps from each printing was measured by following the T543-om-00 standard of the Technical Association of the Pulp and Paper Industry (TAPPI), using a Gurley bending-resistance tester. This device measures the force, in Gurley units, required to bend a specimen by a given distance under controlled conditions. One Gurley unit is equivalent to the force exerted by gravity on 1 mg of mass.

FIBER ANALYSES

Fiber identification was done using TAPPI-recommended staining techniques (Isenberg, 1967:232, 271), and the results were photographed under transmitted light at ×100 magnification. Graff C stain allowed the differentiation of cotton/linen from woody fibers. Cochineal stain was used to distinguish cotton from linen. All samples were examined to evaluate fiber morphology.

Selected stamps from each printing were cut in half and immersed in cuvettes filled with 20 mL of sodium hydroxide (0.05N NaOH) and glass beads. Samples were shaken for 12 hours to repulp the paper for fiber analysis. Using a fiber quality analyzer (Op Test Equipment, Inc.), fibers were then analyzed for length and degree of deformation.

SIZING ANALYSES

The presence and compositions of sizing used in the four printings were determined using the spot tests specified by the Foundation of the American Institute of Conservation (1990). Five samples were tested from each printing, with each group of five chosen to span the range of paper thicknesses observed in a respective printing. As the use of hazardous chemicals was required, all tests were performed under a laboratory hood by a trained chemist. Because some of the indicative stains produced were ephemeral, photographs of results were taken immediately after test completion.

PERMEABILITY

"Oil Gurley porosity" was measured at least five times for each stamp using a Technidyne Profile Plus instrument. Oil Gurley porosity represents the time in seconds necessary to pass 100 mL of air through a constant area of substrate. Although commonly designated "porosity" in the paper industry such measurements actually describe permeability. Porosity is a percentage of a given solid that is occupied by pore space. Permeability is the rate at which a fluid under a constant pressure will flow through a porous solid and represents the interconnectedness of pore space. Longer flow-through times indicate lower permeability, an effect of both fiber size and how densely fibers have been packed together to form the paper's fabric. Highly permeable papers will absorb ink more readily and can lower the resolution of line-engraved printing.

Because the tested stamps were smaller than the instrument's measuring aperture, two layers of polyethylene terephthalate (PET) sheet (100 × 80 mm) were taped together to create a folder through which a circular aperture of 9 mm was cut. The stamp was placed into the PET folder and measurements were taken through the perforated area of 63.6 mm^2.

ANALYTICAL RESULTS

Most collectors approach the identification of the bank note company issues first by printing contractor, then by apparent differences in paper thickness when a stamp is held before a light source. Paper thickness data for each printer/contractor are therefore presented first. Other measurements are then related to these data.

PAPER THICKNESS

Wiley (1915) was the first to determine thicknesses of banknote issue stamps and published measurements of the 3¢ greens produced under each printing contract. The measurements from this study confirm the ranges of Wiley's data for each of the four printings and display the same trends within each printing. Table 2 combines new data with Wiley's, with measurements given in ten-thousandths of an inch.

Two general trends are evident in the raw data. First, the National Bank Note Company's stamps comprise a slightly narrower thickness range than in any of the contracts from 1873 onward. Second, each of the four printings can be characterized by more than one commonly occurring thickness. These are termed modal thicknesses. Note the relative underrepresentation of stamps 0.0031 inches thick (0.0787 mm) within the 1879 and 1881 printings or 0.0029 inch-thick stamps (0.0737 mm) from the 1873 printing.

Displaying these data graphically provides a better understanding of the relative frequency of occurrence of a given thickness. Figure 2 charts the percentages within each size class of the first two printings, as listed in Table 2. None of the resultant curves represents a single normal distribution, that is, a simple bell-shaped curve. Rather, each distribution displays more than one modal thickness. This suggests that under each of these contracts, papers were drawn from more than one population, a notion reflected by collectors' observations (see Table 1). Whether these modes represent more than one paper source, or more than one production run from a single source, cannot be known from these data alone.

National paper thicknesses are bimodally distributed, with modes at 0.0025 and 0.0028 inches (0.0635 and 0.0711 mm, respectively). It is possible that these modes may represent the means of two overlapping normal distributions; more work needs to be done in this regard. Brookman (1966) observed two discrete papers types (see Table 1), which may well have been represented by these modes. Although Wiley's (1915:7) data clearly reveal these modes, he obscured them by characterizing the paper with a single description and a mean thickness of 0.00275 inches (0.0699 mm). Luff (1902) must have observed the thickness range and noted the existence of discrete subpopulations. Scott Publishing Co.'s (2012) descriptions do not recognize discrete paper types.

The frequency distribution of Continental paper thickness is striking in two respects. First, Continental stamps thinner than 0.0030 inches (0.0762 mm) are characterized by the same modes as the National stamps. One is tempted to conclude that the two companies used the same two papers, perhaps obtained from the same supplier. However, stiffness, fiber length, and permeability data refute this; these characteristics will be discussed later.

Second, a third mode at 0.0030 inches appears in the Continental distribution. This mode is also seen in the frequency distribution of 1879 American Bank Note Company stamps (Figure 3). This may be the paper Continental began using in the second half of 1878, which continued in use after American assumed control of Continental's contract and printing operation on 4 February 1879 (Barwis, 2001). Here we have a problem: when off-cover stamps were sorted for this study, how could the "same" paper wind up in two different piles? The answer is that subtle variations do exist in paper translucence within a single thickness grade. Given a large group of stamps 0.0030 inches thick, an objective observer using translucence would call almost half of them Continentals. Another observer would likely produce a very different result. Thus, only covers dated before 4 February 1879 can prove whether a stamp was printed by Continental (Scott Publishing Co., 2012).

Most of American Bank Note Company's stamps printed during the 1879 contract were on paper 0.0032–0.0034 inches thick. This modal thickness has a higher standard deviation than the modal thicknesses in earlier contracts and may suggest quality control issues at the paper mill. Modal thicknesses were narrower during the 1881 contract, in which the primary mode was the thinner (0.0030 inches) of these two papers.

What can we infer from the thickness data? In none of the four printings are paper thicknesses randomly distributed.

TABLE 2. Thickness frequency distribution of 985 3¢ banknote stamps. Data from this study combined with Wiley (1915).

	National, 1870		Continental, 1873		American, 1879		American, 1881	
Thickness (inches)	Number	Percentage	Number	Percentage	Number	Percentage	Number	Percentage
.0019	–	–	1	0.28	–	–	–	–
.0020	1	0.67	1	0.28	–	–	–	–
.0021	1	0.67	1	0.28	–	–	–	–
.0022	1	0.67	7	1.94	–	–	–	–
.0023	7	4.67	3	0.83	–	–	–	–
.0024	9	6.00	17	4.72	–	–	–	–
.0025	27	18.00	65	18.06	1	0.29	–	–
.0026	19	12.67	41	11.39	2	0.57	5	4.00
.0027	24	16.00	61	16.94	2	0.57	5	4.00
.0028	28	18.67	70	19.44	14	4.00	6	4.80
.0029	18	12.0	22	6.11	8	2.29	4	3.20
.0030	7	4.67	43	11.94	56	16.00	37	29.60
.0031	4	2.67	9	2.50	17	4.86	8	6.40
.0032	3	2.00	13	3.61	57	16.29	21	16.80
.0033	1	0.67	4	1.11	53	15.14	10	8.00
.0034	–	–	2	0.56	53	15.14	10	8.00
.0035	–	–	–	–	40	11.43	6	4.80
.0036	–	–	–	–	18	5.14	4	3.20
.0037	–	–	–	–	13	3.71	3	2.40
.0038	–	–	–	–	6	1.71	3	2.40
.0039	–	–	–	–	4	1.14	2	1.60
.0040	–	–	–	–	4	1.14	1	0.80
.0041	–	–	–	–	2	0.57	–	–
.0042	–	–	–	–	–	–	–	–
Total	150	100.03	360	99.99	350	99.99	125	100.00

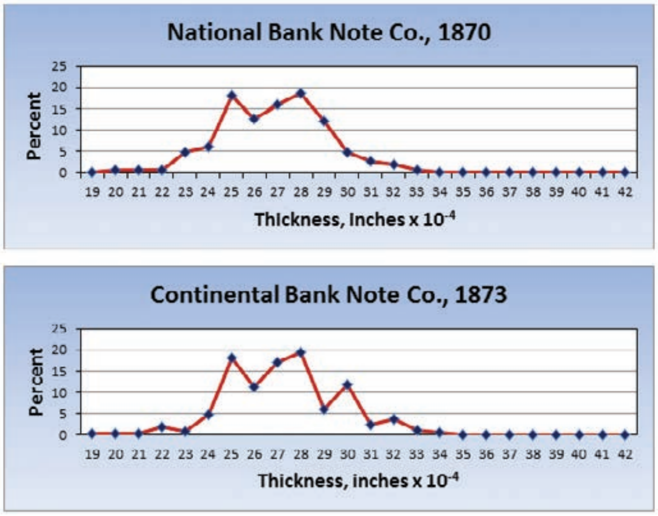

FIGURE 2. Thickness frequency distributions for of the National and Continental Bank Note Companies' 3¢ stamps, based on the data in Table 1.

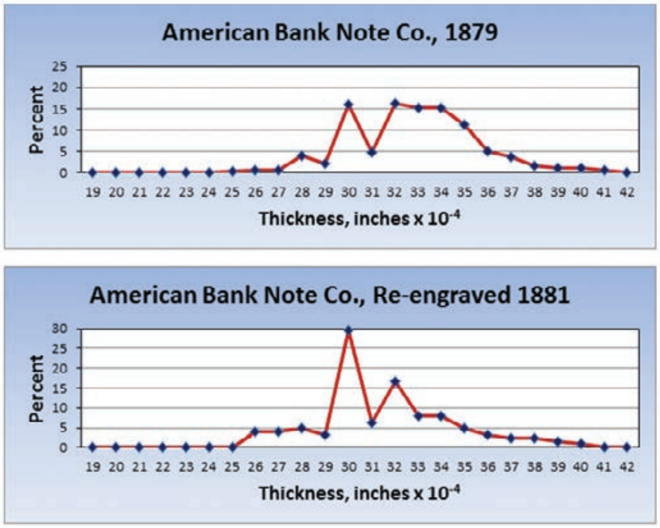

FIGURE 3. Thickness frequency distributions of the American Bank Note Company's 3¢ stamps.

Rather, they cluster around four thicknesses that may represent normal distributions around the means of four discrete populations. Some of the variation is no doubt due to the number of times stamps have been soaked by philatelists in the past 130+ years, as soaking tends to thicken and roughen paper. Soaking some stamps more often than others would tend to increase the standard deviation of a given population.

The thickness frequency data suggest the use of four modal thicknesses with different basis weights. Based on the weights of the 200 stamps used to collect the thickness data, the papers' basis weights would have ranged from 53–56 g/m^2 (0.0025 inches thick) to 69–72 g/m^2 (0.0032 inches thick).

BENDING RESISTANCE

Elastic modulus is the tendency of a solid to deform nonpermanently when a force is applied. It is basically the slope of the stress strain curve in the region of elastic deformation. Because bending resistance (stiffness) of a paper sample is a function of its thickness and its elastic modulus, elastic modulus can easily be determined, since

$$M = EI,$$

where M is bending moment or "stiffness" (bending force in Gurley units), I is moment of inertia (thickness squared times width), and E is elastic modulus.

Sample width can be neglected, since differences in stamp width were negligible. To determine the elastic modulus of a stamp, divide the measured bending force by the square of thickness:

$$E = M/T^2,$$

where T is paper thickness.

The relationships between bending resistance and elastic modulus for each of the four printings are summarized in Figure 4. The correlation coefficients, although not unduly low, may well have been reduced in part by the varying experience each piece of paper has had since its manufacture. Papers with identical thicknesses may have contained different percentages of fines in the pulp resulting from different treatment in the beater, thus widening the range of bending resistances. Sizing concentrations may have varied, which would also lead to greater variation in bending resistance. Variations in ink layer thickness would tend to broaden the range of bending resistances for any given paper thickness. Soaking stamps in water increased paper thickness and therefore decreased elastic modulus.

Table 3 shows that when National and Continental stamps were compared as entire populations, no significant difference was discerned in their elastic modulus. This is consistent with the "snap test" used by collectors for identifying "hard" versus "soft" paper. Although the mean elastic modulus of the 1881 population is lower than the mean of the 1879 population, standard deviations indicate significant population overlap.

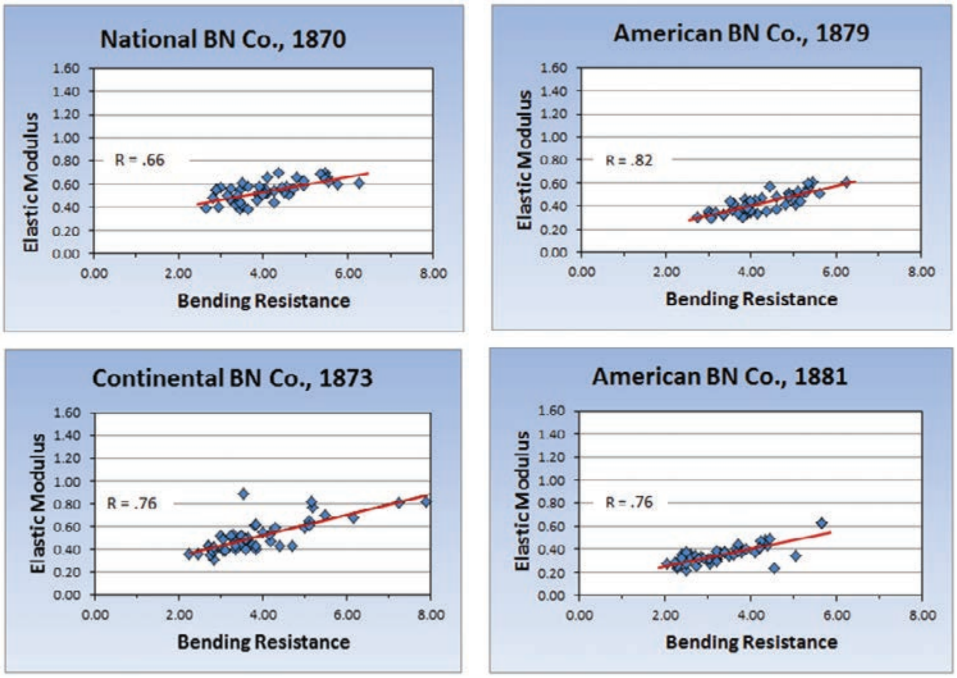

FIGURE 4. Relationship between bending resistance and elastic modulus for the four printings. *R* is the correlation coefficient.

TABLE 3. Elastic modulus data for 1870–1881 U.S. 3¢ stamps without regard to thickness differences within each printing.

Printing	Stamps	Elastic modulus mean/ standard deviation
National, 1870	50	.53/.09
Continental, 1873	50	.51/.14
American, 1879	50	.42/.08
American, 1881	50	.36/.08

A more revealing way to consider paper stiffness is to examine the differences in bending resistance within each printing, based on the modal thicknesses shown in Figures 2 and 3. Table 4 lists the means and standard deviations of these moduli, which are depicted graphically in Figure 5. These data provide the first indication that identical thickness does not prove identical paper. For example, both of the modal thicknesses used by National were stiffer than paper of the same thickness used by Continental. The thinner of these two National papers is 13% stiffer than its Continental counterpart.

Elastic modulus data taken alone indicate no significant differences in 0.0030-inch-thick paper used in three of the four printings, although Continental's displays a narrower standard deviation. This was most likely the paper on hand when the American Bank Note Company assumed control of Continental's operation in February 1879. Paper supplied after depletion of the inherited supply may have been made to a less exacting standard. As we shall see later, sizing played a role in this regard.

In the third quarter of 1878 and January 1879 Continental delivered about 166 million 3¢ stamps to the Post Office Department (Luff, 1902). After February 1879, when American assumed Continental's contract, more than 1.3 billion (6.5 million sheets) of these stamps were delivered prior to release of the 1881 reengraved issue. Therefore, a random sample of Continental or American pre-reengraved stamps on 0.0030-inch paper is about eight times more likely to have been printed after January 1879.

TABLE 4. Elastic modulus data for all stamps that match the four modal thicknesses shown in Figures 2 and 3.

	Elastic modulus mean/standard deviation			
Printing	.0025 inches	.0028 inches	.0030 inches	.0032 inches
National, 1870	.61/.08	.54/.09	–	–
Continental, 1873	.53/.14	.47/.12	.40/.06	–
American, 1879	–	–	.43/.10	.43/.11
American, 1881	–	–	.40/.11	.37/.05

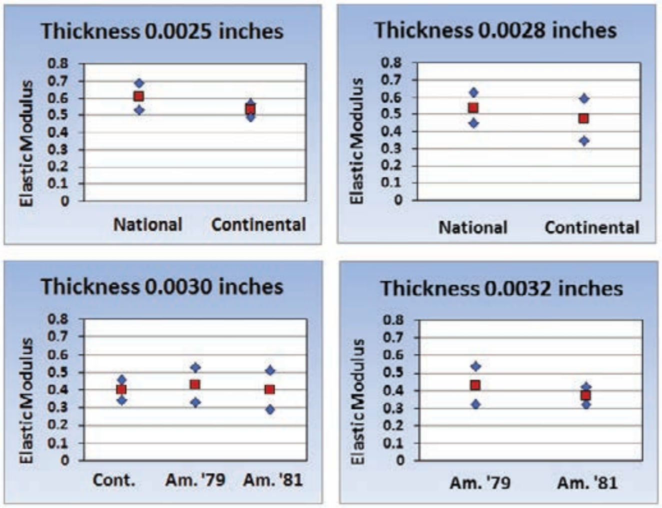

FIGURE 5. Elastic moduli of the four modal thicknesses shown in Figure 3. Red squares are means; blue squares are the standard deviation.

The 0.0032-inch-thick paper used by the American Bank Note Company during the 1881 printing is considerably more pliable, that is, more easily bent, or flexible, than paper of the same thickness used in American's previous contract. The 1881 paper's mean elastic modulus is about 16% lower, and variation about the mean is low (Figure 5). Other analytical results, particularly sizing and permeability, establish differences among papers that demonstrate very similar elastic moduli.

Fiber Analyses

The Graff C staining results are illustrated in Figure 6. Pale red to pink colors indicate cotton or linen. Pale blue indicates bleached cotton. Lignin (wood), which stains yellow, is absent except for a single fiber in the 1879 sample. The cochineal red staining results are shown in Figure 7. Cotton fibers are stained red; notice the absence of fibers other than cotton. In none of the samples was any evidence seen that would support the presence of soda/sulfite pulp in the American Bank Note Company printings, as reported by White (1983:64–65). Occasional stray fragments that stained as lignin are likely to have been detritus inadvertently introduced in the manufacturing process. A few fragments of unidentifiable debris were also observed but are immaterial.

A total of 23 stamps was repulped for fiber size analysis. Although this is an insufficient number to quantify differences among paper types, the data can establish variations between the fabrics of papers with identical composition and thickness. Mean fiber lengths range from 0.532 to 0.732 mm and are shortest in

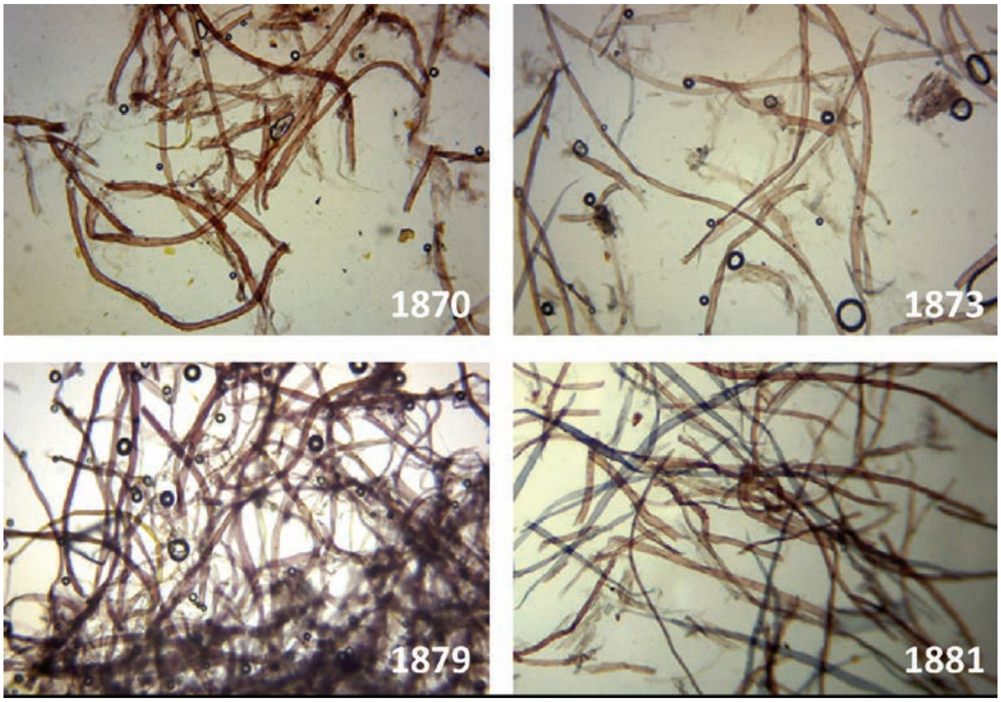

FIGURE 6. Graff C stain for the presence of wood. Pink and pale red indicate cotton or linen. Pale blue is bleached cotton. Yellow fiber (red arrow) may be softwood. Staining and photomicrography courtesy of Robert Hisey.

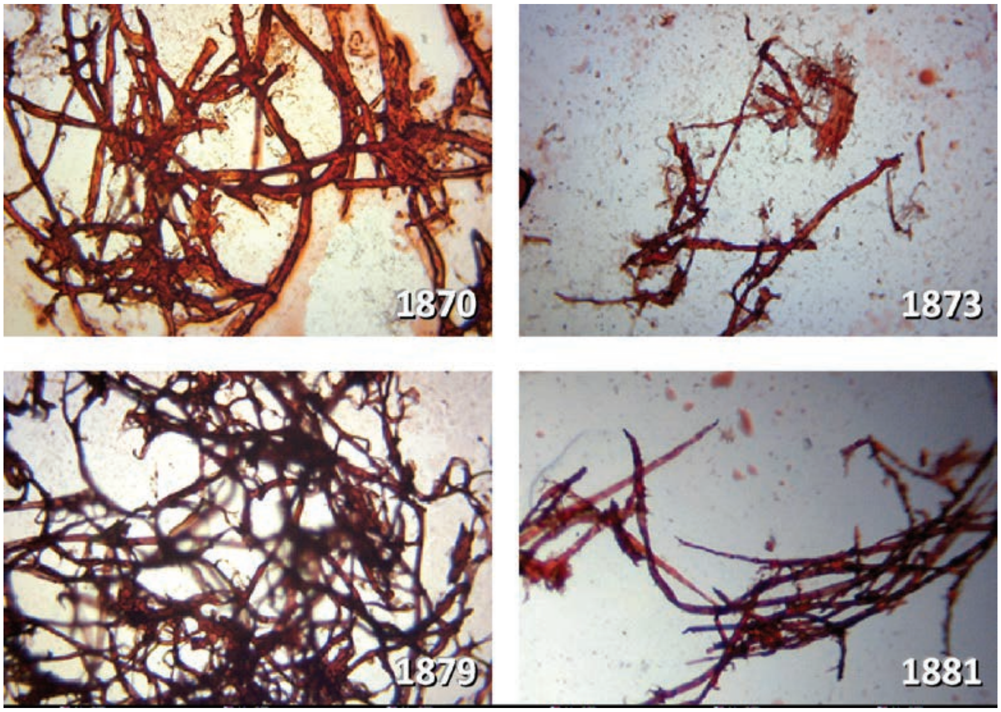

FIGURE 7. Cochineal red stain for distinguishing cotton from linen. Red indicates cotton; violet indicates linen. Staining and photomicrography courtesy of Robert Hisey.

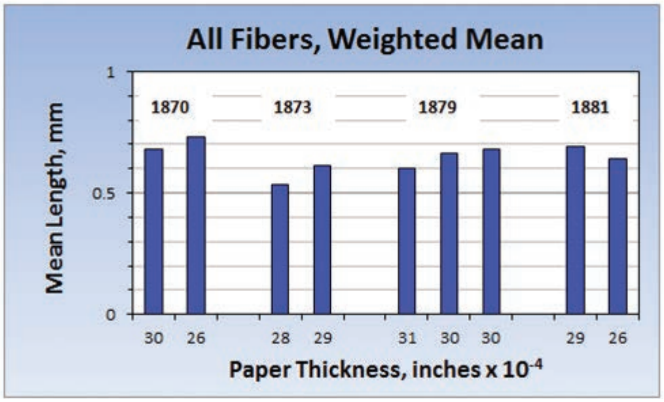

FIGURE 8. Fiber lengths determined from selected repulped stamps. Length data from Pekarovic et al. (2011).

the Continental papers (Figure 8). Shorter fibers suggest longer or more intense beating of the cotton rags used as feedstock for pulp making. This is supported by the observation that cotton fibers in the Continental papers are the most deformed of the four printings (Pekarovic et al., 2011). A fiber size frequency distribution skewed toward the fine fraction may have adversely impacted permeability. Additional work would be required to support this conclusion.

SIZING ANALYSES

Sizing increases a paper's surface strength and stiffness and may provide a smoother finish. Sizing also imparts some form of liquid resistance to the paper or paper fibers by increasing the surface energy or decreasing the porosity of the paper. Sizing that increases surface energy forms a water-repellent film on paper fibers, which inhibits adsorption of water but not oils. This allows a higher proportion of ink to remain on the printed surface and minimizes ink feathering. Rosin/alum was used for this purpose. Because it was added to pulp slurry, usually in the machine chest or the headbox, it is considered "internal sizing," called "beater sizing" in the nineteenth century.

Surface sizing involves immersing dried paper into a sizing solution, an extra step that adds production time and therefore increases unit cost. These sizing types, which include starch and gelatin, form films that decrease paper porosity and permeability.

Five stamps from each of the four printings were laboratory tested for the presence of the three principal sizings used in nineteenth century paper manufacturing: gelatin, rosin/alum, and starch. Standard spot tests were used for these analyses, as summarized in Table 5.

TABLE 5. Stains used to identify paper sizing.

Sizing	Type	Spot test	Result
Gelatin	Internal	Hydroxyproline	Rose red or pink shades indicate gelatin
Starch	External	Iodine potassium iodide	Deep blue to black shades indicate starch
Rosin	External	Raspail #1	Pink to raspberry shades indicate rosin

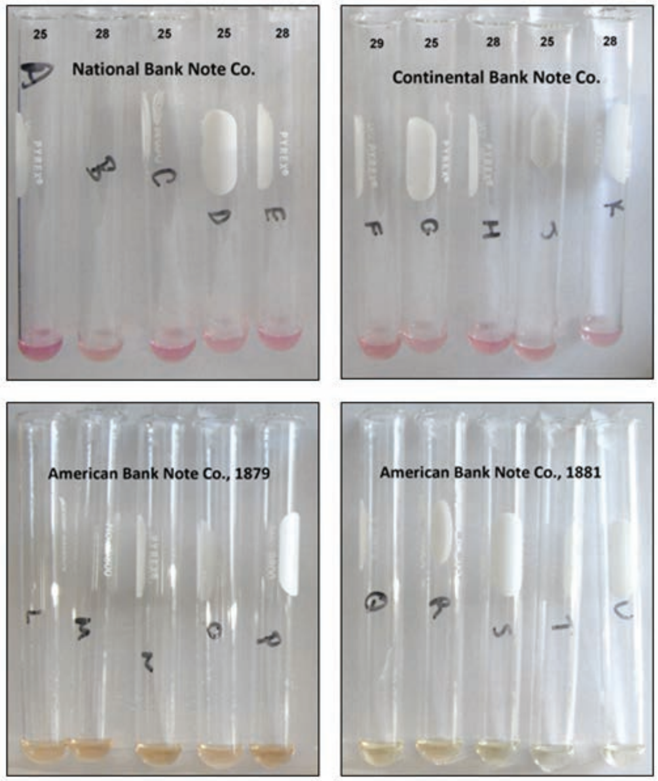

FIGURE 9. Hydroxyproline test for the presence of gelatin. Rose red to pink liquids indicate gelatin sizing. Colorless to brown indicates absence of gelatin. Tests courtesy of Eric Greve, Hope College Department of Chemistry

Gelatin was used as sizing in all of the National and Continental stamps tested. Figure 9 illustrates the typical results. Note that both of the American Bank Note Company printings tested negative for gelatin but responded differently to the hydroxyproline test: yellow-brown results for 1879 stamps and pale straw to colorless for 1881 stamps. Although the hydroxyproline test was not designed to indicate sizing other than gelatin, the fact that the two American Bank Note Company printings responded differently suggests the papers have different chemical compositions. It turns out this is the case, as only the American Bank Note Company's 1879 printing tested positive for rosin. Figure 10 shows the characteristic pink to raspberry stain indicating

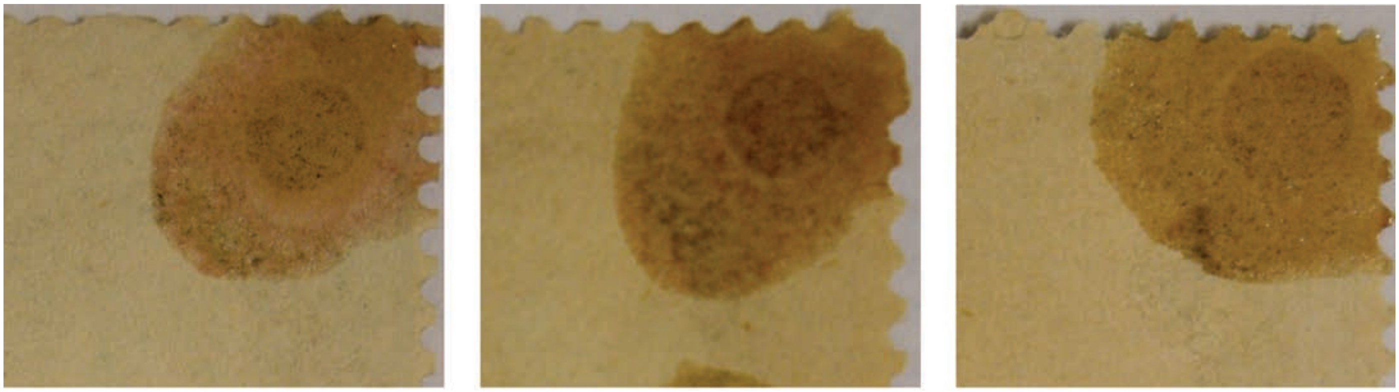

FIGURE 10. Raspail #1 test showing pink to raspberry color halo around the central spot where the stain was applied, a positive indication for rosin. Brown toning of the paper is due to the saturated sulfuric acid used in the stain. Test courtesy of Eric Greve, Hope College Department of Chemistry.

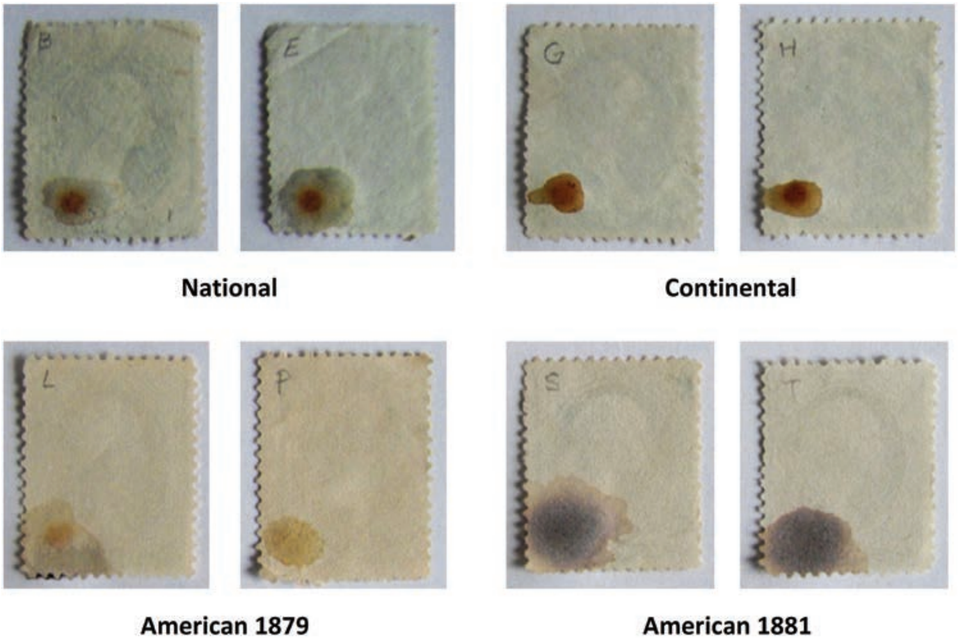

FIGURE 11. Iodine potassium iodide spot test for starch, indicated by a bluish-black stain. Only the 1881 issue tests positive. Test courtesy of Eric Greve, Hope College Department of Chemistry.

rosin, which appears for only 5–10 seconds, after the stain solution is wiped off.

Rosin is never used alone as sizing because it will not adhere to paper fibers but is always used in combination with a mordant, usually alum. Alum is slightly acidic (pH 4.5–7.9), so over time rosin/alum-sized papers can become discolored. Its inclusion in the American Bank Note Company's 1879 printing is probably the reason that these stamps are usually seen with yellower paper than any of the other three printings.

For its 1881 printing the American Bank Note Company switched to paper sized with starch. Figure 11 illustrates the results of the positive spot test, a bluish-black stain. The 1881 issue papers are whiter than the 1879 papers because only starch was used as a sizing.

Why were three different sizings used for the paper to print these issues? The decision to purchase rosin/alum-sized paper in 1879 was undoubtedly an economic decision by the American Bank Note Company, since the change would have lowered their unit cost of paper. When the mill introduced rosin/alum into the slurry, the process of drying the paper and then rewetting it in a sizing tank was eliminated. This would have speeded production, simplified equipment maintenance, and decreased unit labor cost, thus allowing the manufacturer to sell at a more competitive cost.

Permeability

When all four printings are considered as a single population, no discernible relationship exists between permeability and paper thickness (Figure 12). The reasons for this are fairly straightforward. At least five factors influenced the permeability of these stamps.

1. For a given thickness, paper varies in closeness of weave and degree of calendering.
2. For a given thickness, paper varies in the degree of calendering, a process of smoothing by passing through rollers.
3. The composition and concentration of sizings varies considerably.
4. Ink layer thickness varies by a factor of four.
5. Stamps were exposed to a wide range of postuse treatment (soaking history).

A more incisive way to examine these data is to consider permeability variation between the modal thickness groups (see Figures 2 and 3) of each printing. The mean values of elastic modulus for each modal thickness group are plotted against each group's mean permeability in Figure 13. Stiffer paper is toward the right of this chart, and less permeable paper is toward the top. From 1870 to 1879, the trend was toward papers that were less pliable and less permeable. Then in 1881 the American Bank Note Company changed to a more pliable and more permeable paper. It was a less acidic paper than the company had previously used, which is why today the 1881 papers are generally whiter than the 1879 papers. Figure 14, which overlays the chart in Figure 13 with the type of sizing used, paints a clearer picture of the varieties of paper involved.

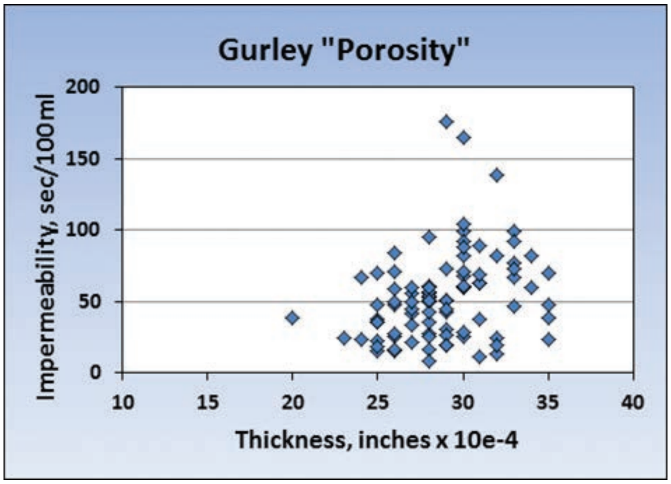

FIGURE 12. Permeability versus paper thickness of the 1870, 1873, and 1879 issues.

Figure 14 shows gelatin-sized papers span a wide range of stiffness and permeability. The stiffest gelatin-sized paper is also one of the thinnest—the 0.0025-inch-thick paper used by the National Bank Note Company. The thicker of the two National papers and Continental's 0.0025-inch-thick paper have very similar stiffness and permeability. The thickest Continental paper—the 0.0030-inch-thick paper used in late 1878 and January 1879—is the most pliable paper used by that company and is the least permeable of all papers used for the 3¢ stamps. Continental's 1878 gelatin-sized paper is very close to the rosin/alum-sized papers in both permeability and stiffness.

Although permeabilities of American's 1881 starch-sized papers are close to the permeabilities of two gelatin-sized papers, the starch-sized papers are far more pliant.

Paper's Impact on Print Quality

All three printing companies constantly dealt with the same challenge facing all manufacturers in managing the tension between minimizing unit production cost while retaining or improving product quality. Intaglio printing required paper pliable enough to be forced into printing plate recesses but strong enough to withstand the printing process and to yield prints not easily prone to wrinkling or tearing. Too much pressure applied in the calendering process might result in stronger paper but weaker resolution of fine line engraving. Less sizing might result in pliability more suitable for gravure printing, but unsized or ineffectively sized paper might cause blurry images from ink bleed.

This study suggests that type of sizing, rather than paper thickness or permeability, was the greatest influence on print quality. Figure 15 shows examples of stamps from each of the regions on the chart in Figure 14. First, considering groups of stamps with similar elastic moduli, compare line resolution of either of the two starch-sized stamps with either of the rosin/alum- or gelatin-sized stamps. The 1881 reengraved stamps tend to look flat, in some instances resembling offset prints. One could reasonably hypothesize that permeability of the reengraved stamps—which is more than double that of the rosin/alum-sized stamps or the Continental 0.0030-inch-thick, gelatin-sized stamps—caused ink to be imbibed by the paper. Indeed, the ink layer is on average slightly thinner on the reengraved stamps. But the entire range in ink layer thicknesses for 200 stamps is only 0.0004 inches, and the range of average ink layer thicknesses varies between printings by only 0.00004 inches.

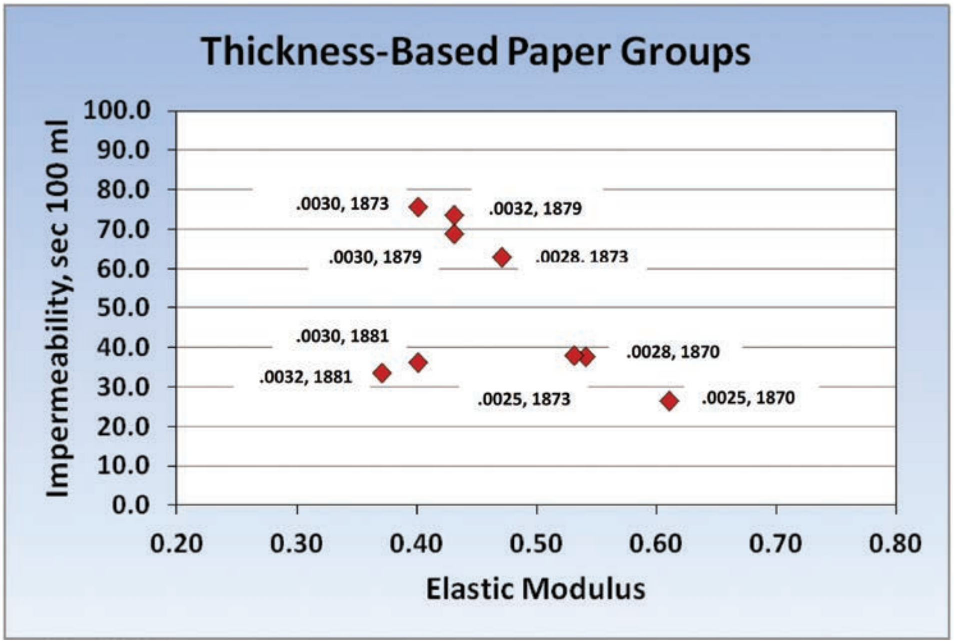

FIGURE 13. Mean elastic modulus versus mean permeability for each of the four modal thicknesses of paper. Note that permeability increases downward on the vertical axis. Paper stiffness increases toward the right on the horizontal axis.

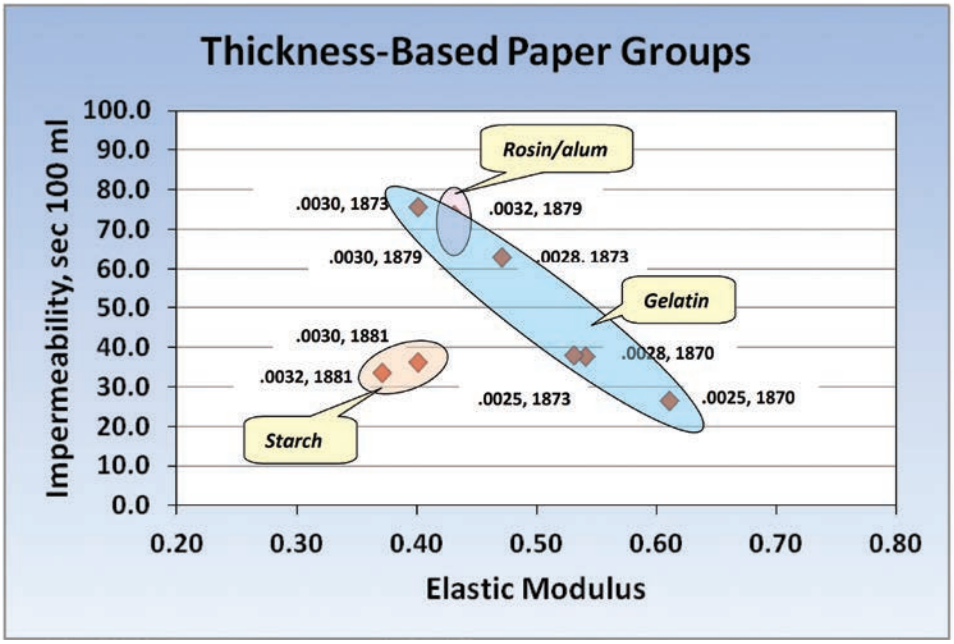

FIGURE 14. Mean elastic modulus versus mean permeability for each of the four thickness groups. Shaded areas enclose papers with the same sizing.

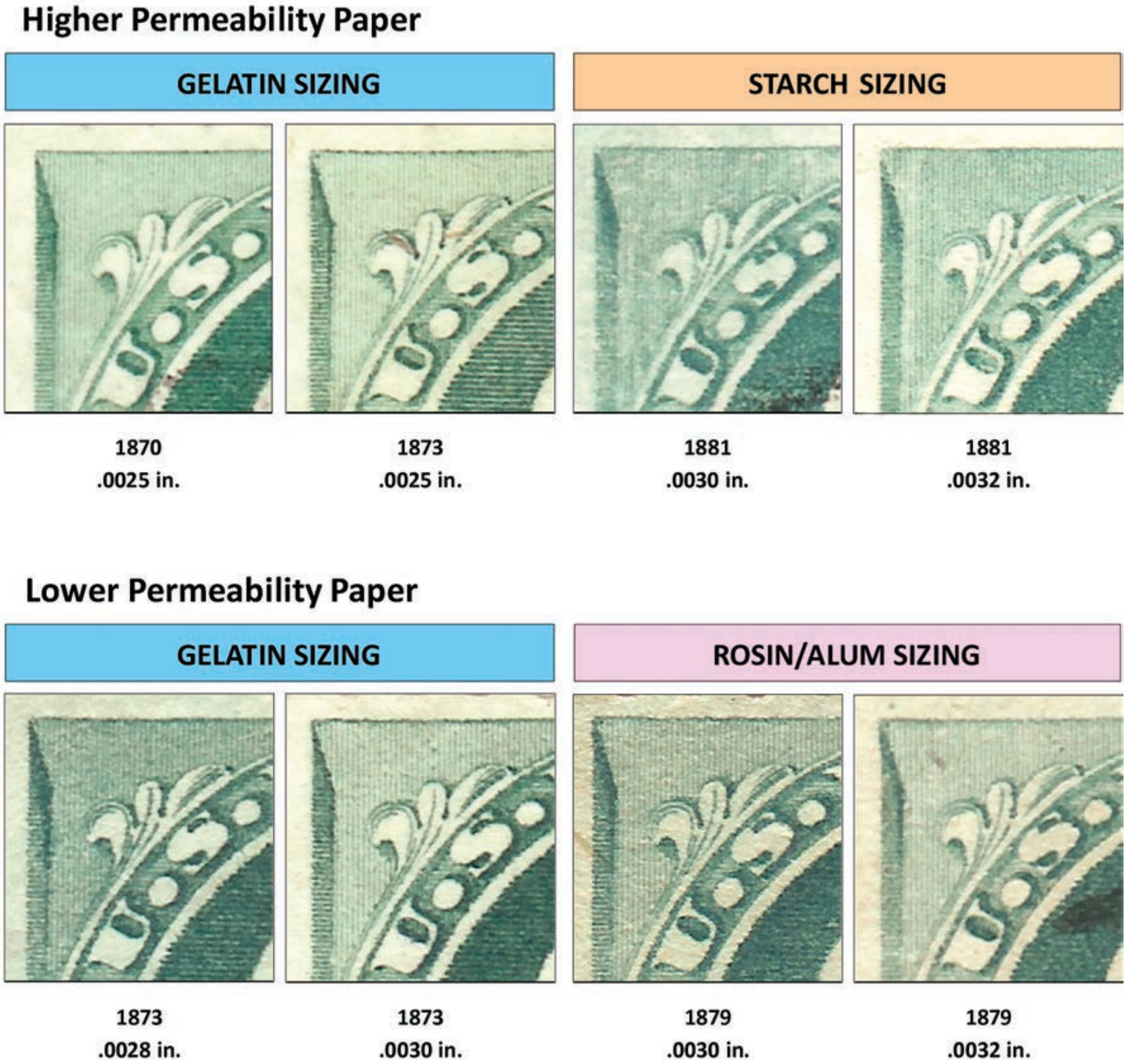

FIGURE 15. The influence of sizing on print quality.

A better way to understand the relative importance of permeability versus sizing is to compare groups of stamps with similar permeability. Compare images of starch-sized stamps in Figure 15 to those from all three modal thicknesses in the lower end of the field of gelatin-sized stamps in Figure 14. The 0.0025-inch-thick paper used by the National Bank Note Company is the most permeable of all the paper types, yet the images on this paper are usually crisp. Weak lines are sometimes seen, but those cases are seldom blurry and are probably just the result of overly aggressive plate wiping. Nor does paper thickness appear to play much of a role in image quality. Continental's images on 0.0030-inch-thick paper are just as finely resolved as those throughout the entire thickness range.

SUMMARY AND CONCLUSIONS

The main types of banknote issue papers traditionally have been defined on the basis of thickness and relative stiffness. This has always been a sensible approach for collectors. After all, what collector wants to run a lab test on a stamp (especially a destructive one) before adding it to his or her album? Yet to understand how banknote stamps were produced and the reasons behind their appearance requires a closer look. Paper that looks the same may perform very differently as an image platform.

The question "How many paper types are there?" can be answered quickly only if the basis for "type" is specified. If one is interested in paper thickness, there are four paper types,

TABLE 6. Summary of paper characteristics of the main types of paper used to print the large banknote issues.

Type	Issue	Printer	Thickness (inches)	Sizing	Average elastic modulus	Average permeability (s/100 mL)
1	1870	National	.0025	Gelatin	.61	26.7
2	1870	National	.0028	Gelatin	.53	37.8
3	1873	Continental	.0025	Gelatin	.54	38.1
4	1873	Continental	.0028	Gelatin	.47	62.9
5	1873	Continental	.0030	Gelatin	.40	75.8
6	1879	American	.0030	Rosin/alum	.43	69.0
7	1879	American	.0032	Rosin/alum	.43	73.7
8	1881	American	.0030	Starch	.40	36.4
9	1881	American	.0032	Starch	.37	33.6

each with a fairly wide range about a mean thickness. If one is concerned primarily with the printing surface as influenced by sizing, there are three types. Table 6 summarizes the paper characteristics of the main types of paper used to print the large banknote issues.

Within each of the 1879 and 1881 issues, the two main modal thicknesses display no significant differences in elastic modus or permeability. Print quality differences are due to different sizings.

The National and Continental Bank Note Companies did not use the same papers. Although both companies used .0025- and .0028-inch-thick gelatin-sized paper, the elastic moduli and permeability of both papers vary significantly between printings. In fact, the thicker of the two National papers is most similar to the thinnest Continental paper.

Continental's thickest paper, the so-called "transitional paper" used in late 1878, was no doubt used by the American Bank Note Company in early 1879 until the supply was depleted. However, this .0030-inch-thick paper was made with different sizing than most paper of the same thickness also used by American.

At no time in either of the American Bank Note Company's two printings was newsprint—cheap paper made from "groundwood"—used for postage stamp production. Groundwood is made by pushing logs against a grindstone, whereas the American papers are cotton. The few wood fragment seen in the Continental and American papers are most likely just debris that found its way into the pulp.

ACKNOWLEDGMENTS

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

Thomas Lera, Jennifer Giaccai, and Nicole Little

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.

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.

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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 (31½ by 59¼ 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 ½ by 19 ¾ inches. The weight per triple ream was 31½ 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, Worchestershire, 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 mm^2 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):

$$u' = \frac{4X}{X+15Y+32}\quad v' = \frac{9Y}{X+15Y+32}.$$

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 ×78 to ×1,600, was used in conjunction with the VSC 6000 software to record close examination details (Figure 5).

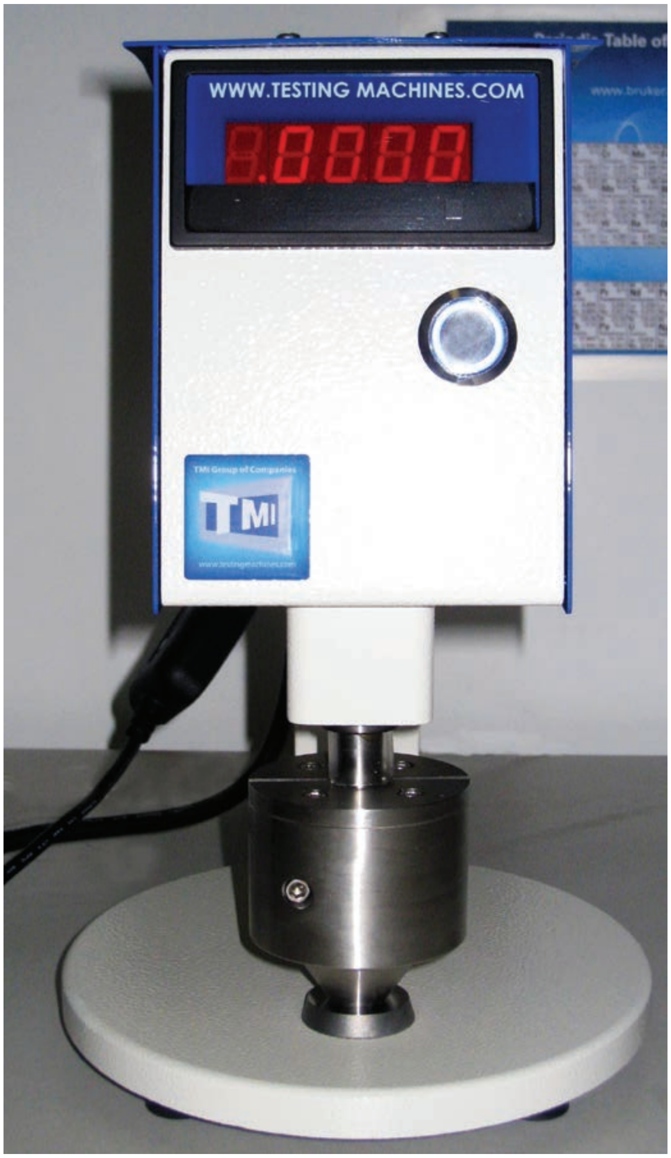

FIGURE 4. Testing Machines Inc. model 49-76-01 micrometer.

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

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 ~0.5 cm^2. Spectra were acquired at a voltage of 40 kV, beam current of 6 µA, 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

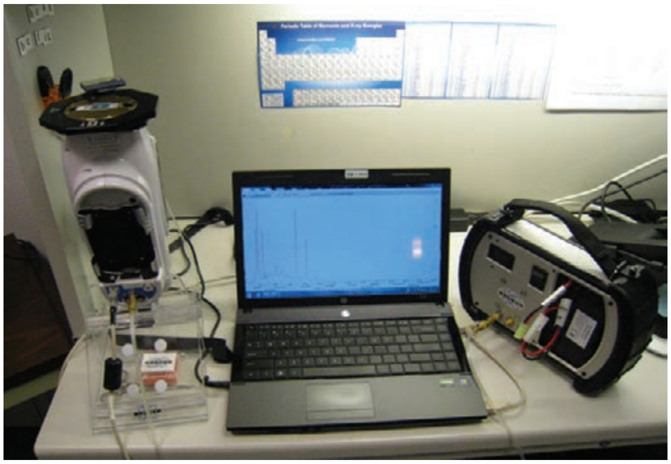

FIGURE 6. Bruker Tracer III-SD X-Ray Fluorescence Analyzer.

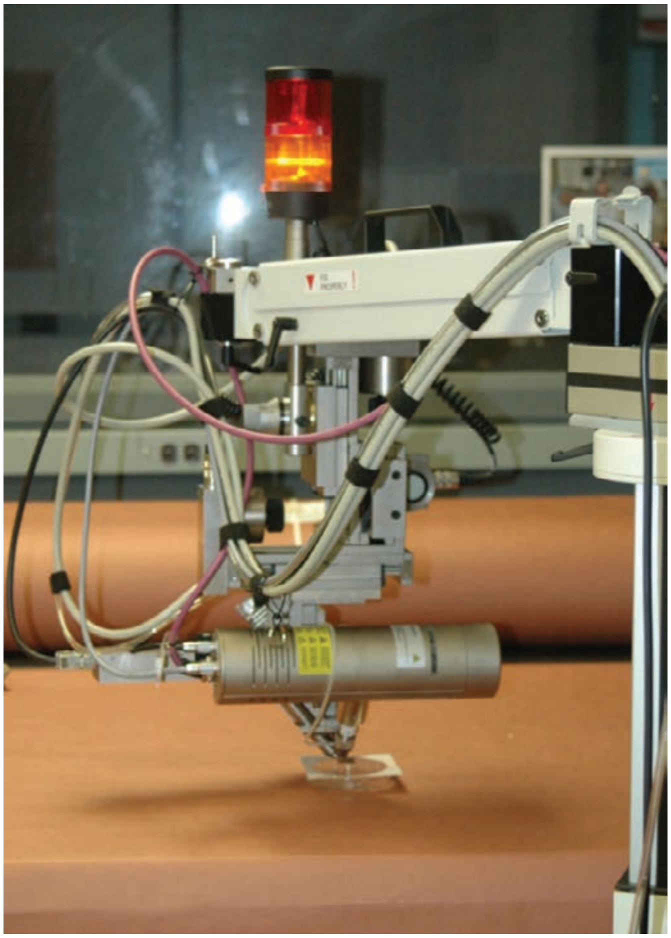

FIGURE 7. Bruker Artax XRF spectrometer.

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 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.

FIGURE 8. Bruker FTIR Alpha.

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.

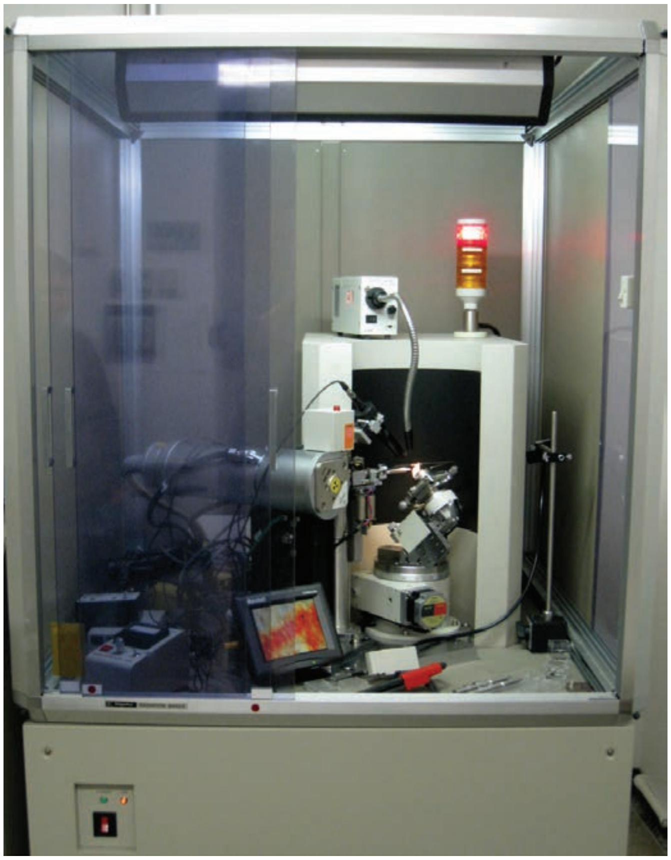

FIGURE 10. Rigaku D/Max Rapid with stamps mounted for analysis.

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

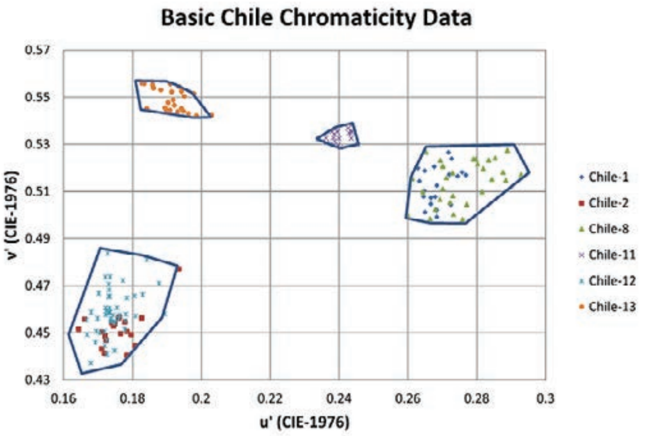

FIGURE 11. CIE 1976 u',v' chromaticity coordinates of the London printing of the Chile stamps.

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)	–	–

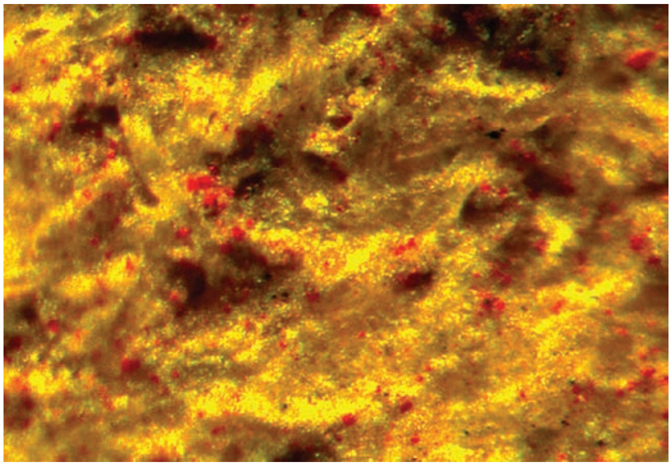

FIGURE 12. Chile number 11 showing the vermilion ink as red spots at ×1,600.

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

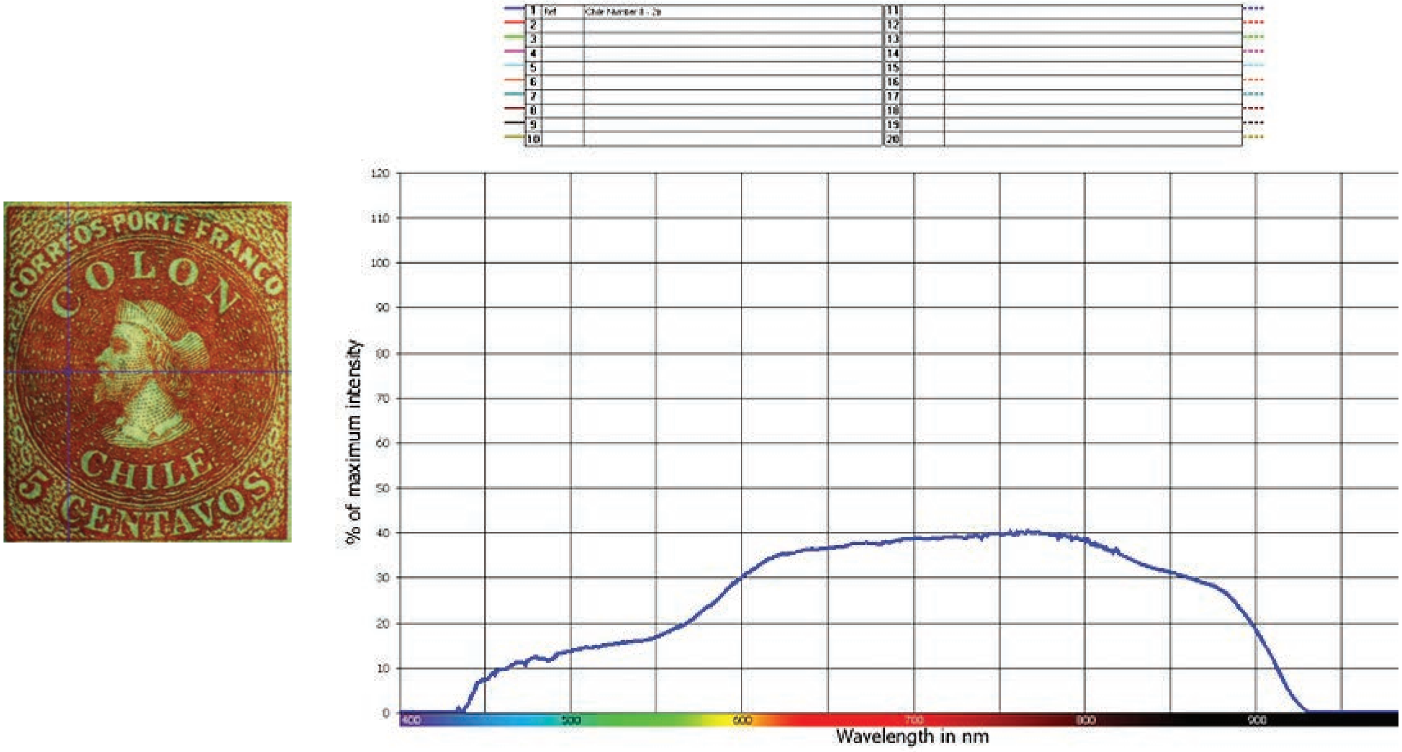

FIGURE 13. The reflectance curve of Chile number 8 showing no organic red dyes present.

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

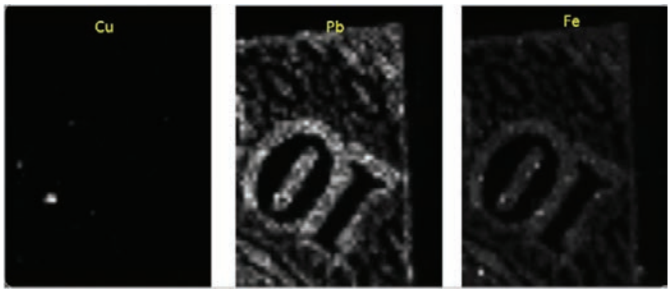

FIGURE 15. XRF map from Chile number 2.

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 addition, Prussian red, $K_3[Fe^{III}(CN)_6]$, 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 $(PbCO_3)_2 \cdot Pb(OH)_2$ 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

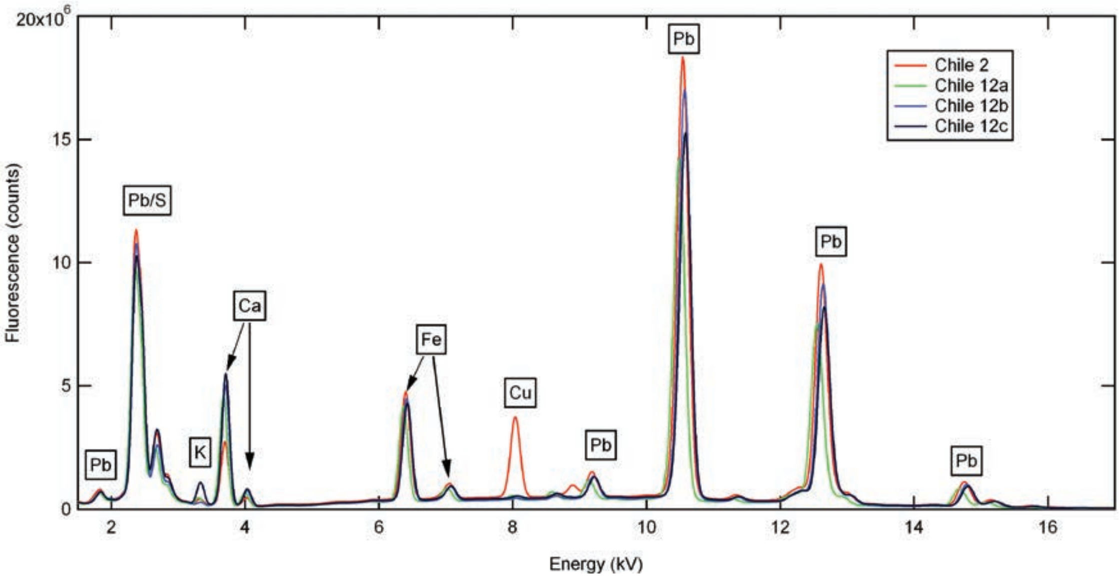

FIGURE 14. Accumulated XRF spectra of blue stamp maps by Perkins, Bacon & Co., 1853 (Chile number 2) and 1861/2 (Chile numbers 12a, 12b, and 12c).

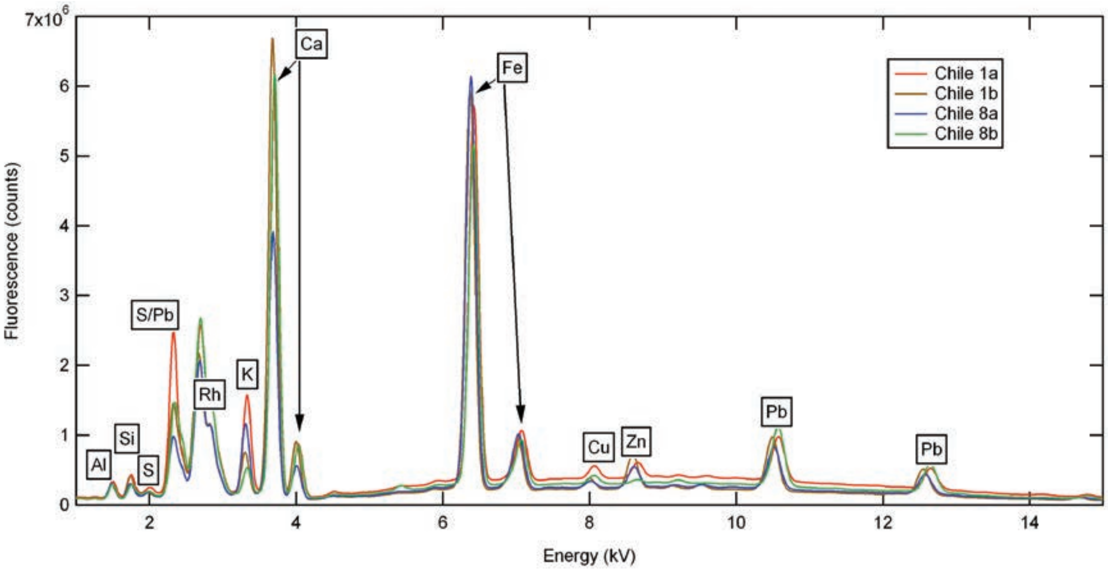

FIGURE 16. Accumulated XRF spectra of red stamp maps from Perkins, Bacon & Co., 1853 (Chile numbers 1a and 1b) and 1855 (Chile numbers 8a and 8b).

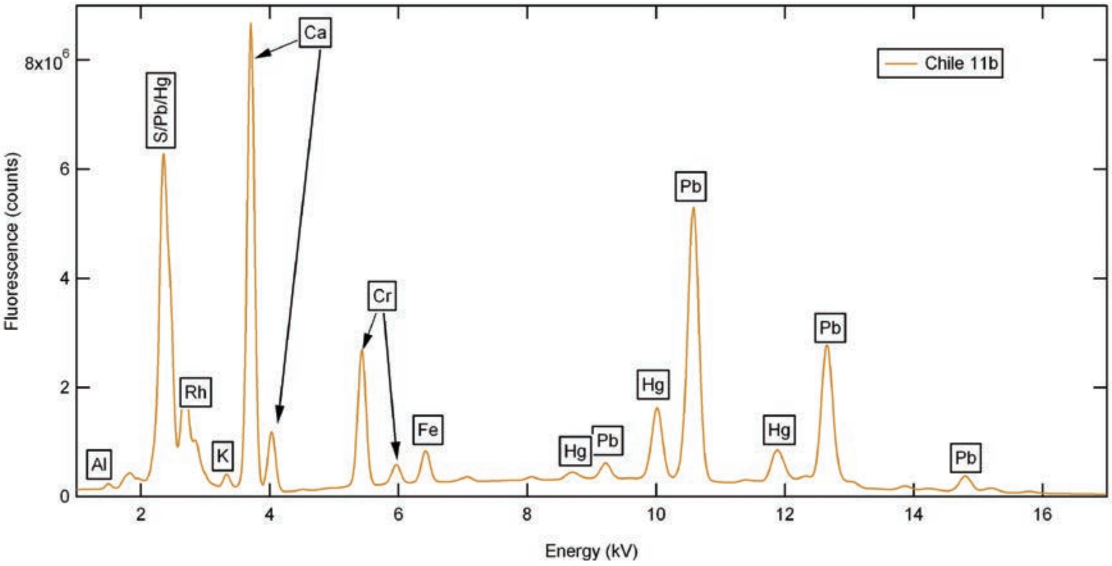

FIGURE 17. Sample of XRF results for Chile number 11.

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, $Fe_4^{III}[Fe_2^{II}(CN)_6]$ and $Fe_4^{III}[Fe^{II}(CN)_6]_3$ and $KFe^{II}[Fe^{III}(CN)_6]$, 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.

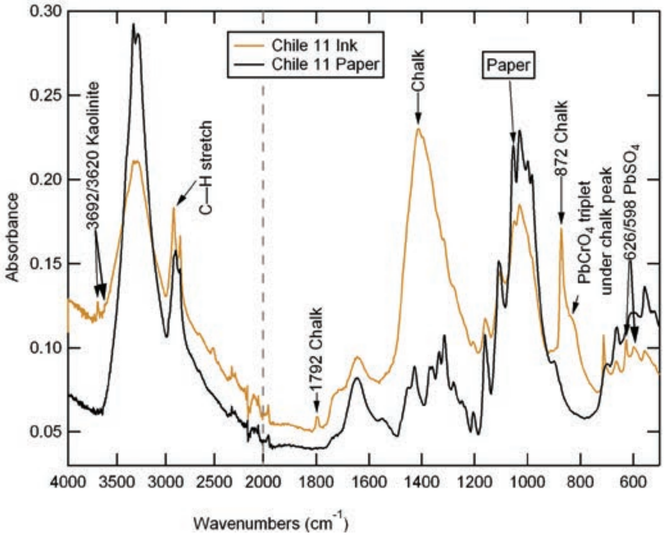

FIGURE 18. Infrared spectra from front and reverse of Chile number 11 showing contributions of paper and ink.

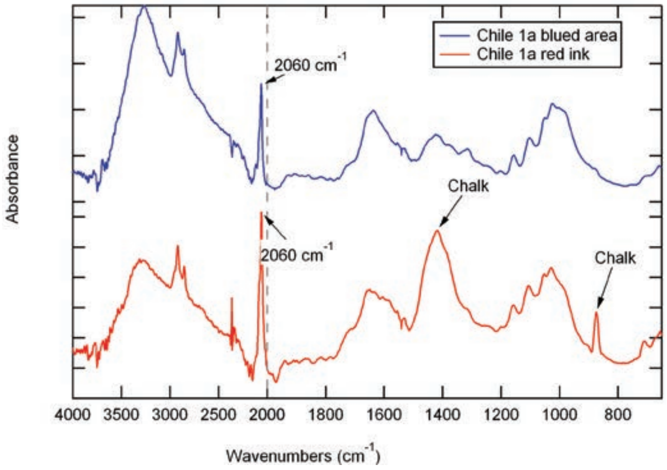

FIGURE 19. The μATR-FTIR of blued ink on 1853 Perkins and Bacon red stamp (Chile number 1a).

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

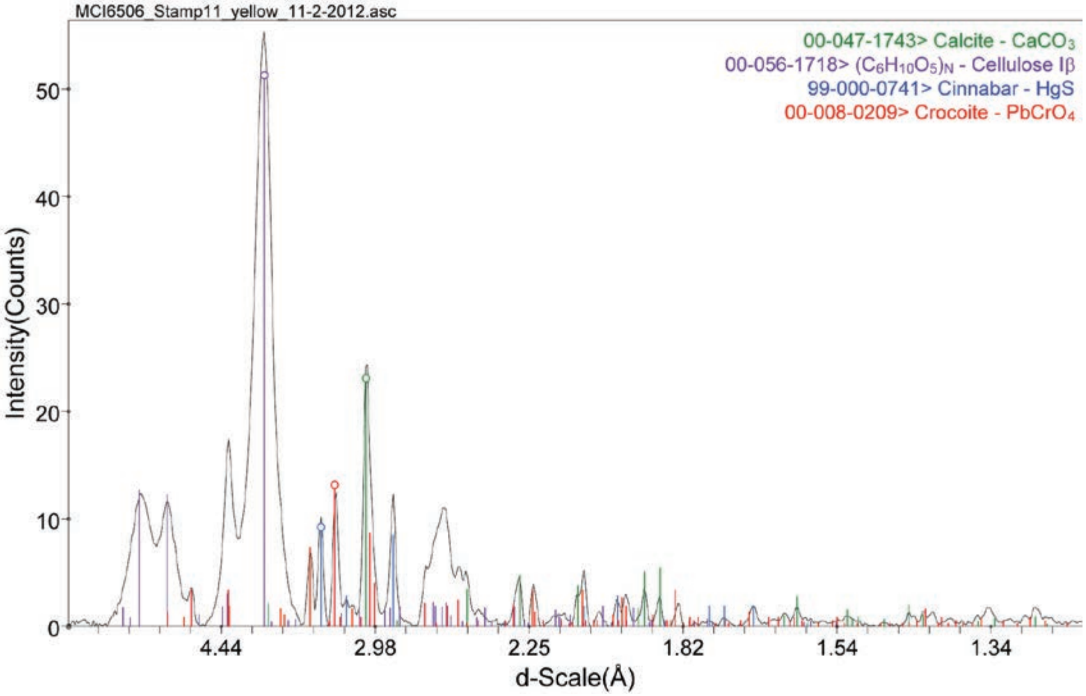

FIGURE 20. XRD data from yellow ink area of Chile number 11 stamp.

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 mm^2) provides overall examination of ink and paper simultaneously, while small-scale analysis (0.01–0.1 mm^2) 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 ($PbCrO_4$). 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 ($Al_2Si_2O_5(OH)_4$) 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 (Fe_2O_3). Unfortunately, the generally noncrystalline 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.

ACKNOWLEDGMENTS

We thank Gary Granzow for his encouragement, support, and research of the Perkins, Bacon & Co. Archives at the Royal Philatelic Society London library and the Hackney Archives,

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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Documenting Science in Philatelic Literature: A New Perspective

David L. Herendeen

ABSTRACT. This paper addresses how scientists in the philatelic community may best document highly technical work in a manner that is interesting and readable for laypersons—stamp collectors. After describing the different scientific aptitudes of philatelists, the paper suggests guidelines scientists might use to reduce complicated concepts to their essence. This is crucial if there is to be an efficient technology transfer of science into the mainstream hobby. Methods posed include a moderation in technical complexity and an increased use of visualization tools, including photos, charts, drawings, graphs, and more. The paper concludes with a discussion of publishing venues for scientific articles to reach the most appropriate audience.

AN UNUSUAL REQUIREMENT

For the past decade, the number of scientific research projects related to philately, and their attendant publications, has been growing steadily. The majority of this research has been focused on various uses of spectroscopy to analyze color, inks, cancels, and paper characteristics. Most of the researchers (e.g., Chaplin et al., 2004; Liston, 2005; Gill, 2007; Odenweller, 2009a; Herendeen et al., 2011; Caswell, 2012) are professors or other trained scientists. This is both good and bad. The good is that the quality of the research is high. The bad is that many of the articles were written by these scientists for scientists.

The transfer of technology into philately has an unusual requirement: the need to communicate highly technical information to laypersons so they understand the basic ideas, importance, and potential applications of scientific results. This paper poses a number of methods to facilitate this transfer.

DIFFERING SCIENTIFIC APTITUDES

The education, experience, and aptitude of each individual usually determine that person's level of interest in science. To set the stage for understanding how to document philatelic science, consider a simple model that includes three widely differing aptitudes for science.

HIGH APTITUDE FOR PURE SCIENCE

Naturally, those with the greatest aptitude for science often enter a scientific or engineering field. Scientific investigation is normally concerned with understanding natural

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phenomena, and it is performed by and for scientists. These scientists must often invent their own "language" to communicate previously unknown concepts. In its purest form, science is an intellectual pursuit. It is not even necessary that there be a practical application of the science. For example, this was initially true for such important discoveries as relativity, quantum mechanics, and string theory.

The pursuit of pure science requires years of study and training. Scientists are dedicated and highly focused. It is not reasonable to expect laypersons either to intuitively understand or to exert the kind of intellectual energy necessary to grasp complex scientific principles. It is therefore counterproductive to communicate with philatelists in "technospeak."

Aptitude for Technology and Engineering

Other individuals with a high aptitude for science study methods for applying pure science to solve "real world" problems. These are technologists and engineers. Once certain scientific principles are proven, they are often used to develop advanced technologies, for example, internal combustion engines, nuclear reactors, and supersonic aircraft. The technologist is not obligated to rederive basic scientific principles at each step but rather is obligated simply to apply them to solve specific problems, invent new devices, or improve upon other devices. This group is able to understand the pure science but always strives to apply it to solving specific problems.

Little Scientific Aptitude

Finally, technologies are transferred to the nonscientific population, those with little scientific interest or aptitude. Perhaps the most famous example of this is Teflon. A material designed for use in spacecraft became a part of the cookware in every kitchen. Users never asked how Teflon developed or why it works. They were simply happy to have nonstick cookware.

This is the most important group to reach if science is to become an accepted part of everyday philately.

Integrating these Groups

These different aptitudes are directly reflected in forensic philately. The First International Symposium on Analytical Methods in Philately (subsequently referred to as "Symposium") has shown that all of these aptitudes exist simultaneously in philatelic research.[1] Indeed, papers were presented representing all three. Most important for the future, several researchers were capable of being quickly trained in the use of forensic equipment. Only a few key concepts may be required to interpret simple results. It is the enumeration and transfer of these concepts that are required to make scientific philatelic analysis successful.

This is where organizations such as the Institute for Analytical Philately, Inc. (IAP) and the National Postal Museum (NPM) are crucial. By bringing together a multidisciplinary group of scientists, technologists, and managers, these nonprofit organizations can facilitate communication and technology transfer between scientists and philatelists.

The premier English-speaking expertizing agencies, the Expertizing Committee of the Royal Philatelic Society London, the Philatelic Foundation (New York), the American Philatelic Expert Committee (APEX), and the Vincent Graves Greene Foundation (Canada) have recently begun integrating forensic equipment into their procedures. This adds further impetus to the need for development of appropriate scientific procedures for philatelic forensics.

THE POTENTIAL AUDIENCE

What, then, is the target audience for scientific writing in philately? Is it the scientific peers of the writer, of which there are few? Or is it members of the entire stamp collecting community, of which there are many?

The answer to these questions should be clear. Unlike academia or industry, the application of science to problem solving is not an end. Instead, it is a beginning that allows new methods and tools to be developed for direct application to philately. As a simple example, consider the comparison of two stamps, nominally the same, that appear to be different colors, not shades. It is easily shown (Liston, 2012) using spectrographic methods that the elemental makeup of the inks is different. Therefore, the stamps are in fact different. That is all a philatelist needs to know. Neither detailed knowledge of the spectrograph, nor deep knowledge of chemistry, nor understanding of excitation of inner shell electrons is needed. If later a layperson wants to be involved in such analyses, then naturally some training will be required. But to benefit or learn from technology it should not be necessary to have a Ph.D. in chemistry or physics.

In summary, the scientist must convey the value of the philatelic component of the research in as direct a manner as possible, using plain English in a way that makes the utility of a technique come alive.

THE IMPORTANCE OF TECHNOLOGY TRANSFER

There are several reasons it is important to direct philatelic science to all philatelists. These are discussed in the following sections.

Philately is a Hobby

Scientists should always keep in mind that philately is, first and foremost, a hobby. For the vast majority of enthusiasts the hobby is about stamps. A smaller percentage of collectors focuses on the usage of the stamps. An even smaller percentage studies the development of other aspects of postal systems. While it is true some philatelists are very serious, not all collectors are. In fact, only a very small portion of the population will ever know or care about hard forensic science.

On the other hand, those who do care, including scholars, expertizers, specialists, and exhibitors, often have an insatiable need to know the truth. This may result from the need to know that a particular item is genuine; it may be to understand the history of stamp production—especially inks and papers—during a certain era; or it may be pure intellectual curiosity. There are perhaps 3,000–5,000 such philatelists around the world based on the numbers of authors and exhibitors. Of these, one estimates that fewer than 2,000 were ever involved in anything at an advanced scientific level either in a university or in industry. At the present time, IAP has about 100 members, slightly more than half of whom are scientists. Those remaining fall into the other categories but are still members of the 3,000–5,000.

The key point is probably 99% of all stamps collectors are not science buffs. Yet many have often wondered about colors, ink, papers, and gum. This group must not be forsaken if science is to play an important role in the future of philately.

Previous Attempts Failed

How many have ever heard of Philatelic Research Laboratories, Inc., Philatelic Research Ltd., or the Arthur Salm Foundation? Ostensibly, these were earlier attempts to bring science into philately. Without going deeply into their history, the first was the brain child of Y. Souren, a major New York stamp dealer from the 1920s until his death in 1949 (Souren, 1939). The second was the creation of another dealer, Roy H. White. It was used as a vehicle for publishing a number of studies during the 1970s and 1980s (White, 1983). The final one, the Arthur Salm Foundation, was created in 1991 by the Collectors Club of Chicago using a donation from the late Arthur Salm and additional funding from the club (Arthur Salm Foundation, 1991).

These three entities shared two traits. First, they were not scientific organizations. The first two appear to have been vehicles for the proprietors to generate business opportunities. This in no way diminishes the fact that their founders were extremely talented at forensic analysis. The third, the Salm Foundation, with an endowment of about $50,000, was formed to conduct research on philatelic products. They used outside laboratories to perform analyses with no apparent interest in developing such technical capabilities permanently for the hobby.

Second, none of these organizations attempted to be inclusive or to develop an ongoing organization that would survive either their creators or their endowments. In other words, they were doomed to expire from the beginning—and they did.

A New Beginning

Why did previous attempts fail? The answer lies with organizations such as IAP and the NPM.[2] IAP was formed in 2009 by a group of philatelists who were both scientifically trained and held senior management positions in industry. This nonprofit corporation is dedicated to funding scientific research in philately and developing new methods that will advance all areas of scientific philately. Equally important to both IAP and NPM is the dissemination of the results of this research.

The long-term goals of IAP also include forming a pool of human resources that can perform research and assist and train others in performing their own research. The NPM forensic laboratory is one place open to researchers.

It is also hoped that the expertizing bodies in the USA, Canada, and Europe will become resources for further research. Thus, it is anticipated that a synergistic relationship will develop that accelerates the integration of science into the hobby.

THE IMPEDIMENTS TO TECHNOLOGY TRANSFER

Exactly what are the impediments that prevent widespread assimilation of new scientific information by the philatelic public? Several of these are discussed in the following sections.

Impenetrable Language

The first potential problem is an article or paper simply contains too much science. Is this possible? Consider a few titles of scientific papers from major journals in other scientific domains:

Analytical Performance in Flow Injection–Simultaneous Multielement–Inductively Coupled Plasma–Optical Emission Spectrometry Employing a Cyclonic Spray Chamber (Hettipathirana and Davey, 1996).

The Notion of a Rational Convex Program, and an Algorithm for the Arrow-Debreu Nash Bargaining Game (Vazirani, 2012).

Only a very small percentage of the population (even of university postgraduates) has any idea what these papers may be about. This is not surprising because the research is published in specialized journals of record in the spectrographic and computing scientific disciplines.

Why would this observation not apply to stamp collectors as well? Consider these titles:

> Characterization of Genuine Stamps, Reprints, and Forgeries of the 1867 and 1868 Issues of the Roman States by Diffuse Reflectance Spectroscopy (Tyler and Peck, 1978).
>
> Fourier Transform Infrared Spectroscopy Applied to Ink Characterization of One-Penny Postage Stamps Printed 1841–1880 (Ferrer and Vila, 2006).

Do you think most philatelists will immediately read these papers? They would perhaps glance through the paper and look at the "pretty pictures." Just maybe, if the figures and graphics convey easily understandable information, rather than data, the reader might actually risk venturing into the text.

Why are titles like these effective?

The "China Clay" Varieties of the 1908–1910 Washington-Franklin Issues (Liston, 2005).

New Zealand: Inks Used for the Early Chalon Heads (Odenweller, 2009a).

They are short, do not try to explain in the title every technique used in the research, and give an easily understood overview of their contents. The author hopes casual readers would not be frightened away before even considering reading the articles.

Too Much Data

After getting past an overly complex title, some research papers proceed to have too much data. Pages full of equations or spectrographs quickly blur the philatelic reader's eye, causing loss of interest. Data should be reduced to the minimum necessary to prove the thesis of the paper. It is not unusual for a research project to generate many, many thousands of data items. But remember, data is not information. Information is the distillation of raw data into trends and conclusions that allow a phenomenon to be better understood and for observations to become knowledge.

As a very simple example, consider the curve shown in Figure 1. This curve represents a physical quantity sampled at more than 400 different conditions for a single stamp. Now, suppose there were a hundred such curves. Would it make sense to show all 100 data sets as separate plots? Of course not. They could all be plotted together, as shown for only 25 curves, in Figure 2. What a mess. Better yet, just the envelope (the upper and lower limits) of the data, and their average, could be shown, as seen in Figure 3. Thus, it has been possible to reduce tens of thousands of raw data items into three easy-to-understand curves showing us the limits and average of the data.

This shows how powerful graphical representation of data can be. This will be discussed in more detail later.

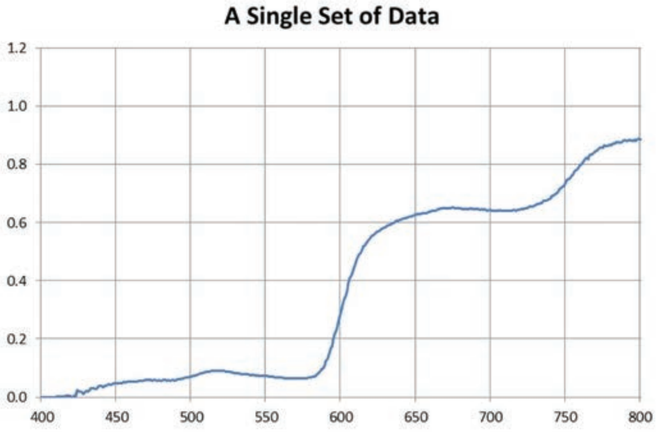

FIGURE 1. A simple curve representing more than 400 raw data points.

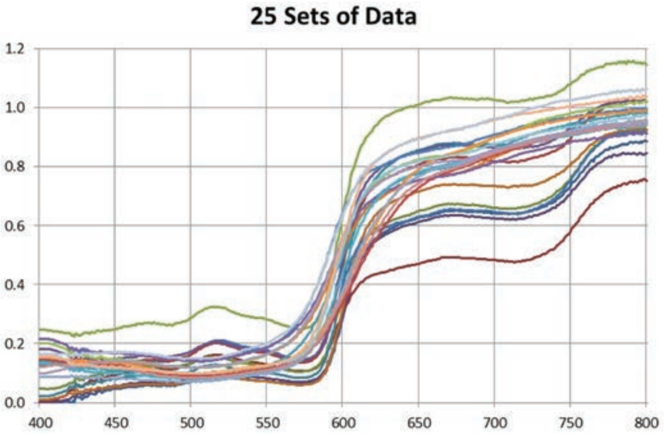

FIGURE 2. Data for 25 measurements on a single plot. Hopelessly useless: too much data, too little information.

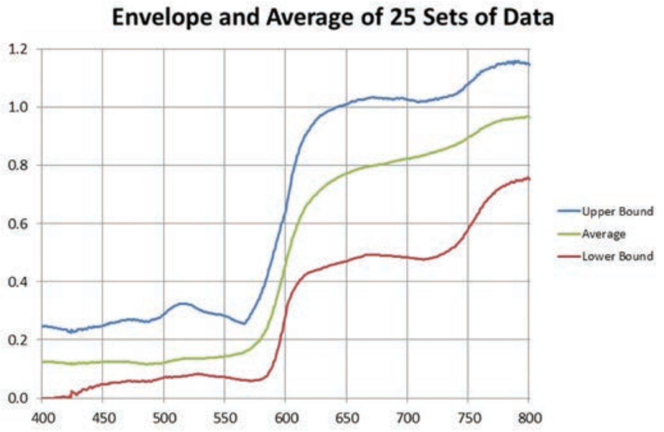

FIGURE 3. Tens of thousands of raw data points reduced to three easy-to-understand curves.

FIXING THE PROBLEMS

As introduced above, the easiest way to make scientific results more understandable is to improve data visualization. Specifically, this means only the data necessary to prove the thesis of the paper should be shown. That does not mean nonsupportive data should be omitted. The results should be understandable to any motivated philatelist. The optimal tools should be selected to present the data, as discussed in the following sections.

Organizing the Paper

One of the easiest ways to improve the readability of a scientific paper is by carefully organizing the presentation of the experiment, equipment, and results. Some ideas are presented in the following sections.

Isolating Ponderous Science

There are cases when a researcher has a great desire to add large amounts of scientific theory, equations, or other embellishments to a paper. Ask if the reader would be better served if this information appeared as appendices that can be skipped by readers who are neither domain experts nor interested. This same observation applies to explaining the type of hardware used to perform forensic analyses. While it is important to specify the equipment used, long lists of technical specifications from the manufacturers' catalog and manual should not overwhelm the thesis and results of the study.

This technique of isolation can greatly enhance the layperson's interest in a paper.

Simplifying Scientific Concepts

Whenever possible, consider simplifying complicated scientific concepts. Some of the current researchers do this successfully. Consider the following description presented by Liston (2012:163):

> The most important aspect of this technique [X-ray fluorescence] is that the elemental composition of the ink remains the same even if there has been a significant chemical change of the ink. For example, oxidation or sulfidization from contaminants in the air or reaction with chemicals in the paper of the album or even light can cause a "color changeling." This is true because the binder in the ink keeps the original layer of ink, with its elements, in place on the stamp even if the chemical nature of the ink has changed.

This description is as simple as it could possibly be. While there may be readers who don't even know what an element is, this still represents, in the author's opinion, an excellent explanation. Researchers should strive for this level of clarity of communication.

DATA VISUALIZATION

In many technical papers, especially those in chemistry, spectroscopy, and physics, much of the data may be represented in figures. There are many different ways to represent data, some of which are described in this section. As seen earlier, the point of using such devices comes from the old maxim "a picture is worth a thousand words."

Photographs

Photographs are a wonderful way to convey knowledge to the reader in a nonthreatening manner. For example, Figure 4 shows a photo of a piece of analytical equipment. This gives

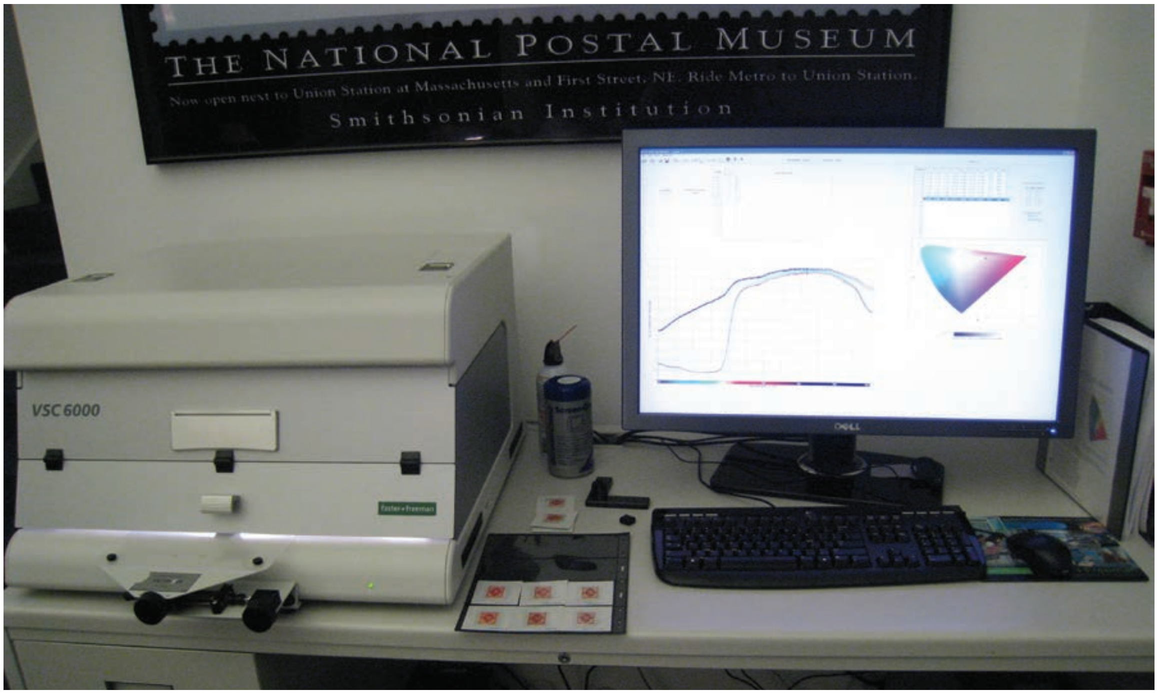

FIGURE 4. Photos of hardware help reduce the mystique of new technology for the uninitiated. From Herendeen et al. (2011, Fig. 9). Courtesy of *The London Philatelist* and the Royal Philatelic Society London.

FIGURE 5. Photos of actual experimentation help illustrate the detail required for high-fidelity results. From Herendeen et al. (2011, Fig. 11). Courtesy of *The London Philatelist* and the Royal Philatelic Society London.

the reader a chance to remove any prejudged mystique and fear of hardware. It is also useful to include one or more reference items so that the viewer gets a sense of the scale of the hardware. Figure 5 shows an experimenter actually dealing with samples during a testing procedure. This kind of photo helps convey the careful organization needed in detailed experimental work.

Drawings and Sketches

Drawings and sketches are often used to reduce complex ideas to a simplified and easily digested form. Consider Figure 6. This little sketch actually describes, in a very simple fashion, the energy dispersive X-ray fluorescence (EDXRF) spectrometer. Given the rather intimidating name of this equipment, the layperson would probably be surprised by the ease with which the principles of this device can be understood. One can trust the scientists who have developed the theory and the engineers who have designed and manufactured the equipment.

Graphs

Another way to make large amounts of data understandable in a single glance is the graph. With the advent of spreadsheet software, the creation of many styles of graphs has been greatly simplified. One use of graphs was previously shown in Figures 1, 2, and 3. Frequently encountered are the spectrographs that are, not surprisingly, the result of spectrographic analyses. A classic example is shown in Figure 7. This graph represents many thousands of samples taken by the EDXRF to determine the chemical elements in a sample.

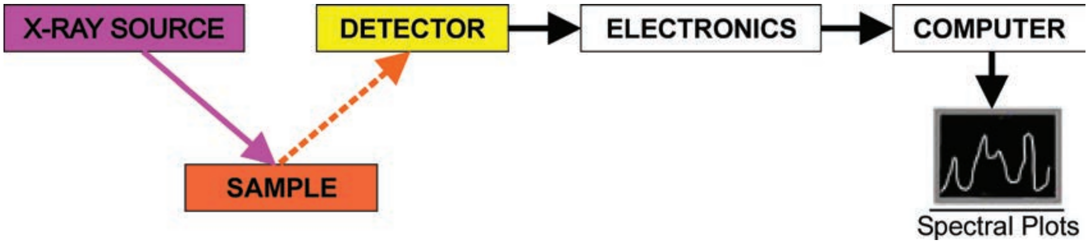

FIGURE 6. An example of a drawing or sketch used to provide a simple description of a possibly complex process. This is the logical design of an EDXRF spectrometer.

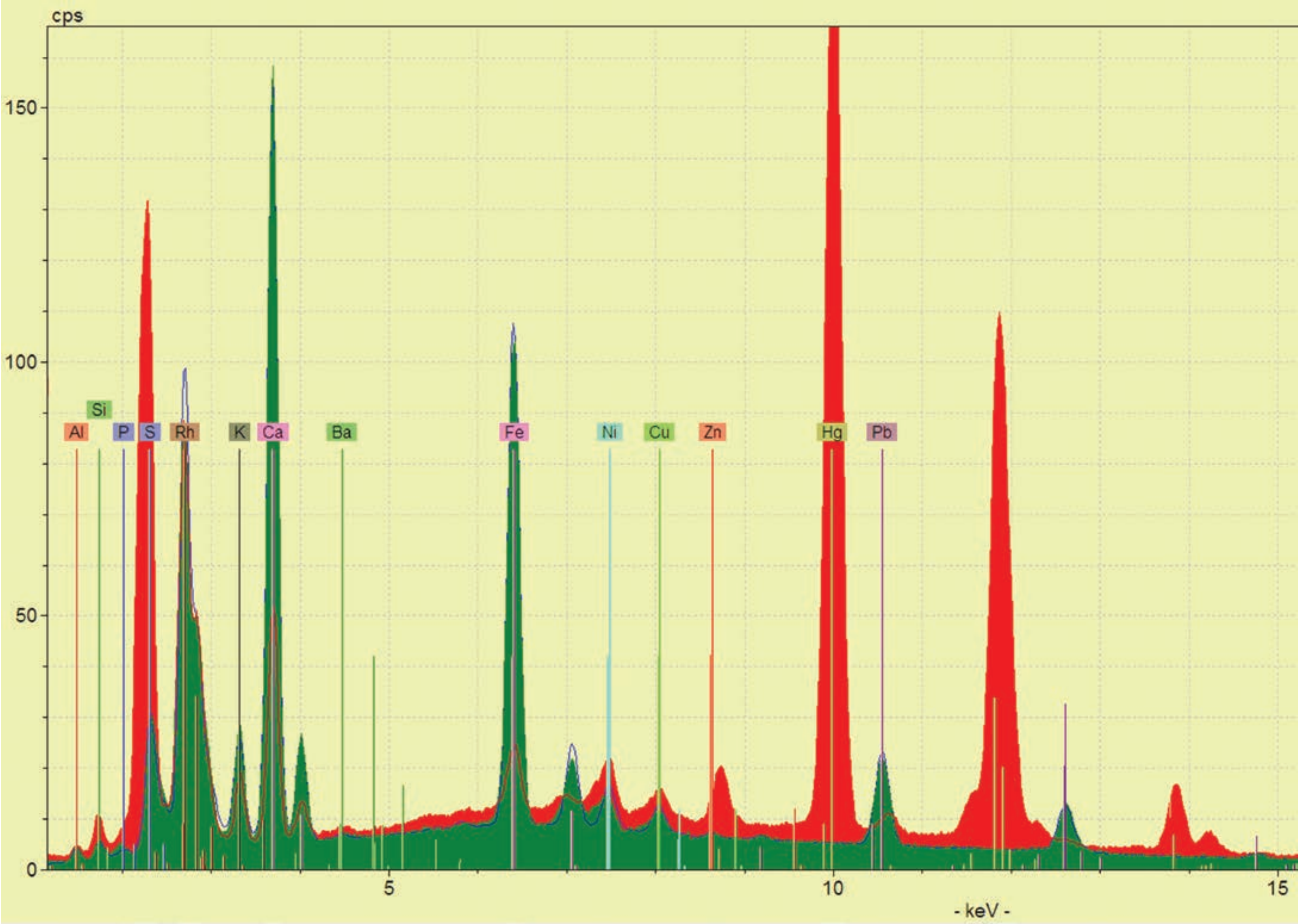

FIGURE 7. A typical spectrograph showing two different ink compositions (one in green, the other in red) based on simple elemental analysis using EDXRF. This allows the differences in ink composition to be easily discerned as the chemical elements are labeled.

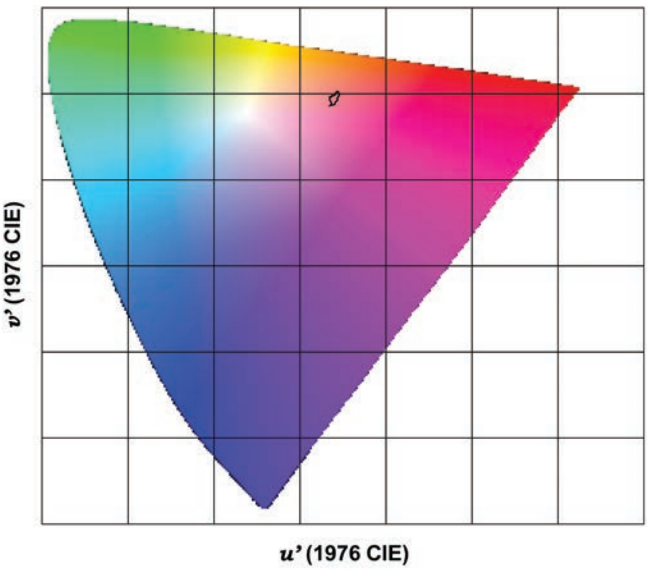

FIGURE 8. An example of a chart providing a simple view of a complicated concept. From Herendeen (2011, Fig 2). Courtesy of *The London Philatelist* and the Royal Philatelic Society London.

Charts

Charts include bar, pie, scatter, area, surface, and many others. Generally, these charts allow different classes of data to be readily viewed and understood. For example, typically, bar charts are used to illustrate quantities such as sales by quarter or height by age of children.

There are many more exotic types of charts. Consider Figure 8. This is what is called a chromaticity diagram. It is very difficult to express what is shown in words alone. Generally speaking, the small area noted by the arrow describes the various shades of color (red-orange) within the spectrum of colors defined by a specific color model of a large group of stamps. These words simply do not convey as memorable a concept as what is present in the drawing.

The flowchart is another useful device. It is often used to show the logical flow of a process. An example is shown in Figure 9.

Tables

Sometimes an author wishes to present actual numeric data. This may be done in tables. Normally, such tables, to be useful, have only a few numeric values in them.

For example, Table 1 shows a portion of a table that shows how an expert identified colors based on their chromaticity coordinates (Herendeen et al., 2011, Table 1:111). The author believes tables tend to be much more useful in humanities research than numeric-based research because there are usually very large quantities of data that are being reduced to draw specific conclusions. Mind-numbing tables of raw data seldom communicate such conclusions effectively.

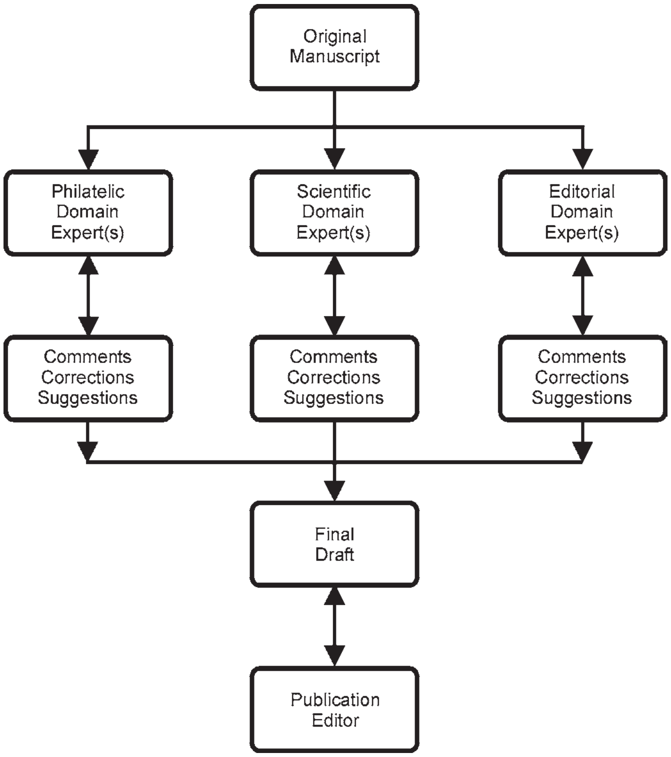

FIGURE 9. Logical flow of the ideal manuscript peer review process.

TABLE 1. Allocation of color categories (extracted from Herendeen, 2011, Table 1).

	Chromaticity coordinates		
Sample	***x***	***y***	**Expert allocation**
P_1	0.3381	0.4948	H2
P_2	0.3370	0.4940	H2
P_3	0.3433	0.4993	H3
P_4	0.3351	0.4917	H1
P_5	0.3364	0.4926	H1
P_6	0.3395	0.4943	H1

OUTSIDE READERS

One of the most important aspects of scientific research is to have one's work reviewed by outside readers. The principal reason to use outside readers is to make certain that no simple errors have been made and that the paper is understandable. All authors are subject to the same modes of failure. For complex subjects that take prolonged periods of research, the scholar is often so embedded in his work that a wide perspective is lost. Experience has shown that it is possible for small, but very important, facts to be overlooked.

Odenweller (2012b:132), in an editorial in the *Collectors Club Philatelist*, wrote

> On occasion we have been asked if it would be a good idea to "referee" the articles that appear in the way they are done for scholarly journals. Usually this is not practical, either due to time constraints or for finding the appropriate referee, since the author is likely to be one of the most likely to know the subject best. Still, we do try to ask for input from other specialists when it is possible, sometimes while the article is being processed for print. If this is the case, and an answer is received too late for the issue, we can entertain a "response" article for the next.

The author, as one who has edited several philatelic specialty journals, understands the origin of this position. Few philatelic publications have the luxury of an article "backlog." The production of even a quarterly journal requires a constant scouring of a society membership for material. When using a review process of any type, there is usually a time lag that can easily be intolerable.

The second objection, the difficulty of finding domain experts to act as referees, is not necessarily true, as amplified in the next section.

Philately is Different

Scientific papers relating to philately are different from those in many other disciplines because there are three domains of expertise that come into play with philatelic science. The first domain is the science itself. Thanks to the advent of IAP and a growth in scientific analyses, especially those related to spectroscopy, there is a growing pool of talented researchers qualified to objectively review such manuscripts. The second domain is the philatelic one. The author believes that there is always at least one additional expert capable of critiquing and fact-checking a research manuscript. This is similar to finding professors to serve on a Ph.D. committee for a candidate who is already working at the state of the art in some scientific field. This is, in fact, a common occurrence. The third and final domain is a reviewer who can determine if the manuscript is conveying useful information to readers who may not have a strong scientific background. Such reviewers will most often be scientific managers who were fighting this battle for many years when trying to convey extremely difficult scientific concepts to upper management in the corporate world.

The Procedure

The logical flow of the actual procedure for the ideal peer review process is shown in Figure 9, an iterative procedure including feedback loops between the reviewers and the author and later between the author and the publication editor. It is this feedback that improves publication quality.

A Real-World Example

To see how this works, consider the author's article on the inverted frame postage-due stamp of Labuan (Herendeen, 2006). This project was quite large in scope. Without getting into great detail, this study required contacting many collectors, dealers, and expertizing groups around the world; combing thousands of auction catalogs; and scouring many journal articles and stamp publications. After two and a half years, the basic research was completed. The article itself was multidisciplinary in nature. It included a detailed history of the stamps, a comprehensive census, the use of computer graphics to reconstruct multiples, and statistical analysis to estimate the number of errors that may have been printed.

So how does one have such an article "refereed?" For this paper, several domain experts in British colonial stamps were used, a university professor was used to check the statistical formulation, and several philatelic editors were used to insure the quality of the manuscript.

Does such a procedure take time? Most certainly, but this time is well worth it when it yields a superior result.

WHERE TO PUBLISH SCIENTIFIC PHILATELY

Once the scientific study has been documented, exactly where should it be published? There are two aspects to consider when making this decision. The first is whether a sufficient audience of philatelists exists with enough scientific background to gain important insight from one's work. The second is the philatelic subject matter.

The Collectors Club Philatelist

The *Collectors Club Philatelist* (*CCP*), until recently under the editorship of Robert P. Odenweller, is an excellent venue for publishing scientific articles. There are several reasons for this. First, Odenweller (2012a) noted that the *CCP* plans to be a leader in the publication of quality scientific articles. During the 2000s, a fair number of important articles have appeared (e.g., Liston 2005, 2012; Lera, 2012). Odenweller's successor, Gene Fricks, has indicated that he will continue supporting scientific articles. Fricks is a professional scientist and will be a great editor for scientific work.

The *CCP* has a circulation of more than 900 and a good penetration into major public libraries. This makes it easy for philatelists to access materials published in it. Others may be able to find material on the IAP Web site,[2] at the American Philatelic Research Library,[3] or through the recently formed Global Philatelic Library (Walton, 2012).[4]

The London Philatelist

The honorary editor of the *London Philatelist* (*LP*) is Frank Walton. The *LP* is the literary organ of the Royal Philatelic Society London (RPSL). To date, only a modicum of scientific analysis has been presented in the pages of the *LP*. However, the RPSL now has a Video Spectral Comparator 6000 and an XRF spectrometer on order. These should become a source of more articles based upon optical and chemical spectroscopy in the near future. With a worldwide circulation of more than 2,100, this publication is also ideal.

The American Philatelist

The *American Philatelist* (*AP*) is the monthly magazine of the American Philatelic Society. The editor is Barbara Boal. Many years ago, the *AP* editorial policy changed its tone, leaning more to historical and thematic articles than hard-core research. Nonetheless, scientific articles have appeared occasionally over the past four decades (e.g., Tyler and Peck, 1978; Glazer and Dow, 1983; Hanneman and Hintze, 1991; Bell and Blackett, 2012).

The obvious plus for the *AP* is that it has a circulation of more than 32,000 monthly, and many philatelic scientists are members.

Major U.S.-Related Journals

The major U.S. specialty journals *The Chronicle* (U.S. Philatelic Classics Society, circulation 1,200), *The United States Specialist* (United States Stamp Society, circulation 1,800), and *The Confederate Philatelist* (Confederate Stamp Alliance, circulation ~700) have large circulations and a significant number of practicing and retired scientists. For research related to U.S. material, these may be the best venues for articles. They have already published some of these, such as White (1989a, 1989b, 1989c). These are all high-quality productions with good color. *The Postal History Journal* would generally be most appropriate for research relating to verifying markings, cancels, and other indicia on covers.

Specialty Journals

Most specialty journals have relatively low circulations, e.g., 100–600. With the exception of *Philatelica Chimica et Physica*, the journal of the Chemistry and Physics on Stamps Study Unit, these specialty groups also tend to have relatively few scientists as members.

Professional Technical Journals

One should consider submitting work to the various professional journals as well as the philatelic ones. There are several reasons to do this. First, it raises the stature of analytical philately in the eyes of those who feel that these publications are a validation of the worth of research. Perhaps more important, there is an opportunity to expose large numbers of scientists, all of whom have analytical capabilities, to the fact that there are philatelic mysteries to be solved. Readers may think of novel approaches to solving problems exposed by published papers.

This is not an easy road, and perhaps current researchers in academia will be able to help pursue this area.

The Book

Finally, you can write the great book on a particular philatelic subject. For example, works that have wonderful scientific content include Glazer (1994) and Odenweller (2009b).

The problem with a philatelic monograph is that it is virtually impossible to tell from the title that there is any scientific content. Also, generally speaking, the circulation of monographs in today's world is modest, and their cost is often significant. This is not a good combination for making maximum penetration to the potential technical audience.

Web Publishing

The final possibility is to create an electronic article that is hosted by a Web site. IAP will do this for members and nonmembers without charge. By using this vector, the number of possible worldwide readers will be increased dramatically.

THE POWER OF GRAPHICS

The author requests that readers of this paper now go back to the beginning. By looking only at the section headings and graphics, do you know what the paper is trying to convey? If yes, then the paper is a success. In no, the author will go back to the drawing board.

CONCLUSION

This paper has described the difficulty scientific philatelists may have in communicating scientific results to nonscientific philatelists. It has identified a set of problems and suggested a number of solutions to them.

It is hoped this new proposed publishing paradigm will allow the current renaissance in scientific enquiry to flourish rather than wilting like other earlier attempts.

ACKNOWLEDGMENTS

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NOTES

1. The First International Symposium on Analytical Methods in Philately was held at the Smithsonian National Postal Museum, 12–14 November 2012. It was organized by the Institute for Analytical Philately, Inc.

2. More information on the Institute for Analytical Philately, Inc. may be found at http://www.analyticalphilately.org. For the National Postal Museum, see http://www.postalmuseum.si.edu (accessed 18 July 2012).

3. To see what the APRL offers and to use the online catalog, see http://www.stamps.org/About-the-Library (accessed 18 July 2012).

4. Through its portal, the Global Philatelic Library has access to 19 different philatelic libraries in the USA, United Kingdom, Australia, Canada, Germany, and Norway. See http://www.globalphilateliclibrary.org (accessed 18 January 2013).

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Infrared Spectroscopic and X-Ray Diffraction Studies of the Typographed Confederate 5¢ Stamps

Harry G. Brittain

ABSTRACT. It has been determined that X-ray diffraction (XRD) is a highly useful analytical tool for study of the paper used in the printing of postage stamps of the Confederate States of America. Through use of the technique, one may differentiate among different types of paper that were used in the printings, primarily through a characterization of the inorganic salts used as sizing and filling agents. When combined with attenuated total reflectance (ATR) sampling, Fourier transform infrared (FTIR) spectroscopy can be used to study the pigments used in the printing inks, and with comparison with suitable reference standards, FTIR-ATR spectra can be used to identify the pigments used in these inks. The utility of XRD and FTIR-ATR will be illustrated using the 5¢ blue typographed postage stamps featuring the portrait of Jefferson Davis that were issued by the Confederate States of America during 1862–1863 (Scott CSA-6 and CSA-7). Through study of appropriate examples, it has been found that FTIR-ATR spectroscopy can be used to distinguish between the printing ink used by the De La Rue Company (London, England) and by the Archer & Daly Company (Richmond, Virginia). It has also been found that XRD can distinguish between paper supplied by De La Rue and paper obtained locally by Archer & Daly. The nondestructive protocol that has been developed is to first use FTIR-ATR to determine whether a given stamp should be classified as being either CSA-6 or CSA-7. Subsequently, XRD is used to confirm that a CSA-6 stamp is printed on London-sourced paper or whether a CSA-7 stamp is printed on London-sourced or Richmond-sourced paper.

INTRODUCTION

The first stamps printed by the Confederate States of America (CSA) were produced by the Hoyer & Ludwig and the J. T. Paterson companies using a lithographic process (Dietz, 1929: chapter 5). It was always the intent of the Confederate postmaster general, John H. Reagan, to print stamps using steel engraving whose quality would equal those printed by the United States Federal government, but logistics prevented him from achieving his goal until the spring of 1863 (Kimbrough and Bush, 2011:90–98).

In October of 1861, the Confederacy sent Major Benjamin F. Ficklin to England to contract for various supplies needed by the CSA Post Office Department to produce its own high-quality stamps (Dietz, 1929: chapter 7). The CSA needed to acquire a sufficient quantity of printed stamps to hold them over until it could obtain the plates and materials for production of locally printed stamps. Accordingly, an agreement was reached with the Thomas De La Rue & Co., Ltd., in London for typographed stamps and plates of two denominations of stamps. The first shipment did not make it through the Federal blockade, but the second shipment was placed aboard the blockade runner *Giraffe*

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(later renamed the *Robert E. Lee*), which successfully evaded the blockade and landed its cargo in Wilmington, North Carolina, in February of 1862 (Kimbrough and Bush, 2011).

The central motif of the 5¢ blue stamp (Scott catalog CSA-6) (Scott Publishing Co., 2012) is a portrait of Jefferson Davis that was designed and engraved by Jean Ferdinand Joubert De La Ferte (Kimbrough and Bush, 2011:103–107). The stamps were printed from one 400-subject electrotype plate and were delivered in half sheets of 200 divided by a vertical gutter into two panes of 100 each. The imperforate stamps were printed on thin, white, woven, hard-surface paper with colorless gum, and the impressions were clear and distinct. Because these stamps were printed by De La Rue in England, these stamps are known as the "London Print" issue.

Using the De La Rue plates brought through the blockade, more 5¢ stamps were typographed in Richmond, Virginia, by Archer & Daly, so these stamps are known as the "Richmond Print" issue. Two kinds of paper were used for the Richmond printings, one being the thin, white, woven, hard-surface paper imported from England (which in this paper will be identified as CSA-7L) and the other being an inferior paper manufactured locally (which will be identified in this paper as CSA-7R). In addition, the ink used in the printing of the typographed Richmond prints was obtained locally, and this resulted in a range of apparent colors that spanned all shades of blue.

Although the Richmond printings were printed from the same De La Rue plate, one can generally distinguish them from the London printings by the overall coarser impression of the image. However, it can be somewhat difficult to distinguish the early Richmond prints from the later prints, especially when the stamps were printed on the imported De La Rue paper. Since these distinctions can sometimes be subtle, it was appropriate to develop analytical techniques that could be used to establish a protocol for the differentiation of London prints (CSA-6) from Richmond prints (CSA-7) as well as the two Richmond prints (CSA-7L and CSA-7R) from each other.

In order to determine what types of forensic analysis could be used to differentiate the various typographed 5¢ blue Jefferson Davis, authentic reference stamps (shown in Figure 1) were studied using Fourier transform infrared (FTIR) spectroscopy coupled with attenuated total reflectance (ATR) and using X-ray diffraction (XRD). It was found that the elemental components of the printing ink could be characterized using the FTIR method, while the composition of the paper could be deduced

CSA-6
(London print)

CSA-7L
(Richmond print on De La Rue paper)

CSA-7R
(Richmond print on Richmond paper)

FIGURE 1. Typographed 5¢ blue Jefferson Davis stamps that served as references during the course of method validation.

using the XRD method. Subsequently, substantial numbers of stamps of all three types were analyzed using the same technologies to verify the rugged nature of the analytical procedure.

TECHNOLOGY PRIMER

Since the work is heavily based on forensic analytical technology, it is appropriate to first provide an outline and basis for the methodologies used.

X-Ray Diffraction

The various techniques associated with X-ray diffraction (XRD) deal with physical properties related to the crystalline nature of solids (Brittain, 1995: chapter 7). The external examination of crystals reveals that well-formed crystals are completely bounded by flat surfaces, and it has been established that the surfaces of crystals depend critically on structural arrangements of the atom molecules in the crystal. In fact, when high-quality crystals are available, one can use single-crystal XRD to determine the exact structure and intermolecular bonding in the crystal.

The basis for the XRD effect lies in the fact that the three-dimensional pattern of atoms or molecules in a crystalline solid is such that it can act as a diffraction grating to light (i.e., X-rays) having wavelengths of the same order of magnitude as the spacings between planes of atoms or molecules in the crystal. All X-ray diffraction techniques are ultimately based on Bragg's law, which describes the diffraction of a monochromatic X-ray beam impinging on an atomic or molecular plane. Parallel incident rays strike the crystal planes at an angle (denoted as θ) and are then diffracted at the same angle. The observation of reinforcement requires that the path difference of the impinging beam (i.e., the distance between molecular planes, known as the d spacing) be equal to an integral number of wavelengths. The scattering angles can be correlated to the spacings between planes of molecules in the lattice by means of Bragg's law:

$$n\lambda = 2d \sin\theta,$$

where n is the order of the diffraction pattern, λ is the wavelength of the incident X-ray beam, d is the distance between planes in the crystal, and θ is the angle of beam diffraction.

Stamps, of course, are not crystals, but either their ink or underlying paper can contain crystalline components capable of diffracting X-rays. As a result, the technology used to study the XRD of powdered solids can be easily applied to the study of the crystalline materials present in a stamp.

To measure the XRD of a powder, a randomly oriented sample is prepared so as to expose all the planes of a sample and is then irradiated with a monochromatic X-ray beam. In one measurement mode, the scattering angle is determined by slowly rotating the sample and using a scintillation counter to measure the angles of diffracted X-rays with respect to the angle of the incident beam (Klug and Alexander, 1974). The XRD pattern will therefore consist of a series of peaks detected at characteristic scattering angles. To measure the XRD pattern of a stamp, one conducts the same experiment but simply situates the stamp so that its surface is in the same plane as would be used for a powdered sample.

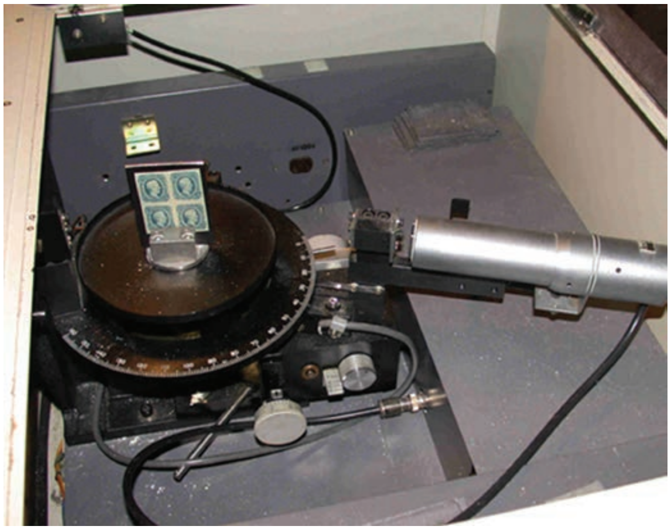

FIGURE 2. Interior view of the X-ray diffractometer, illustrating the goniometer and the mounting relationship of a studied stamp with the X-ray source (extreme left of the figure) and the detector (the cylindrical object at the right side of the figure). Image courtesy of the author.

Since every crystalline compound is defined by a unique structure, each will yield a unique and characteristic XRD pattern. As a result, the XRD pattern of a substance can be taken as a "fingerprint" of that substance and can therefore be used for qualitative identification of materials. In practice, one obtains the XRD pattern of reference materials, and a positive identification of that material in an unknown sample can be made if it can be determined that the two diffraction patterns are equivalent.

In this work, XRD patterns were obtained using a Rigaku MiniFlex powder diffraction system equipped with a horizontal goniometer operating in the $\theta/2\theta$ mode. The X-ray source was nickel-filtered Kα emission of copper (1.54184 Å). As shown in Figure 2, the stamps were pressed against the sample holder in the goniometer and were scanned over the range of 3.5–40° 2θ at a scan rate of 0.5° 2θ/min. The intensity scale for all diffraction patterns was normalized so that the relative intensity of the most intense peak in the pattern equaled 100%.

Infrared Spectroscopic Analysis

The patterns of intramolecular motion existing in molecules are characterized by repetitious oscillations of atoms about the center of gravity of the molecule, and these correlated motions are termed the vibrational modes of the molecule. Energies associated with the lowest-energy vibrational modes of a chemical compound will lie within the range of 400–4,000 cm^{-1}, and transitions among these modes therefore fall into a region of the electromagnetic spectrum denoted as the midinfrared region. Infrared absorption spectroscopy is a highly useful technique for the physical characterization of solids, and its utility has been amply demonstrated in a wide variety of applications (Brittain, 2006: chapters 7 and 8). For a variety of experimental reasons, the acquisition of high-quality infrared absorption spectra appropriate for the characterization of substances is now almost universally performed using Fourier transform technology. As a result, the technique is referred to as FTIR spectroscopy.

The principles underlying the absorption of infrared energy by molecules can be understood using a simple example. Consider a bent molecule consisting of three atoms, such as water (H_2O), which would be capable of undergoing a variety of bending and stretching motions. For example, a symmetric mode of water would be the simultaneous motions of the end hydrogen atoms and the central oxygen atom in a symmetric stretching of the bonds. Also possible is an asymmetric stretching vibration arising from compression of one bond and a stretching of the other bond as well as a bending vibration consisting of an opening and closing of the bond angle.

However, in order for these molecular motions to be initiated, the water molecule must absorb infrared energy, and that energy must exactly match the energy required to effect a change in the pattern of molecular motion. Since every molecule possesses only a finite number of molecular vibrational modes, a molecule can absorb only a finite number of discrete infrared energies. Each of these will correspond to the energy of a particular vibrational mode of the molecule, and the sum total of infrared absorptions is termed its absorption spectrum.

One of the outcomes of spectroscopic theory is that the energy of a particular vibrational mode is determined primarily by two factors. One factor is the strength of the intermolecular bonds involved in the vibration, and the other factor is the mass of the atoms involved. Consequently, the vibrational energy of every molecular group will fall within a fairly narrowly defined range, and correlation tables that relate molecular properties and absorption energies are well developed (Socrates, 2001). One often sees infrared spectra divided into two regions, one being termed the “fingerprint” region (400–2,300 cm^{-1}) where groups of similar atomic masses undergo absorption and the other being termed the “high-frequency” region (2,500–4,000 cm^{-1}) where hydrogen is one of the atoms undergoing absorption.

While the energy associated with a particular molecular vibrational mode can be roughly understood, the exact value of that energy will be strongly influenced by the rest of the molecule whose motions couple into the vibrational mode of interest. As a result, every molecule will have its own characteristic and defining absorption spectrum, and this enables one to use infrared absorption spectroscopy for identity testing. The conduct of an infrared identification study proceeds in much the same manner as does an XRD investigation. The FTIR spectra of appropriate reference materials are obtained, and these are compared to the spectrum of the unknown sample. When equivalence in peak energy between reference and sample is obtained, one can be assured that the peak in the sample can be attributed to that of the compound constituting the reference.

Probably the most useful sampling method for FTIR spectroscopy is that of attenuated total reflectance (ATR). Here, infrared radiation is passed through a crystal at an angle that causes the light to undergo total internal reflection. At each reflection, the radiation penetrates a small distance beyond the crystal surface so that the internally reflected energy will be attenuated at those frequencies corresponding to changes in molecular vibrational states of whatever is held in physical contact with the crystal. The advantage of the ATR technique is that it requires effectively no sample preparation, since one simply clamps the analyte onto the surface of the crystal with moderate pressure to ensure a sufficient degree of optical contact. The internal reflectance process does not permit the infrared beam to pass very deeply into the sample, so the ATR sampling method permits one to effectively study only the outermost layers of a sample.

In the present study, Fourier transform infrared absorption spectra were obtained at a resolution of 4 cm^{-1} using a Shimadzu model 8400S FTIR spectrometer, with each spectrum being obtained as the average of 40 individual spectra. The data were acquired using the attenuated total reflectance sampling mode, in which the samples were clamped against the ZnSe crystal of a Pike MIRacle™ single-reflection horizontal ATR sampling accessory. This particular ATR sampling device enables one to study an approximate 1 mm^2 area of a stamp and is illustrated in Figure 3.

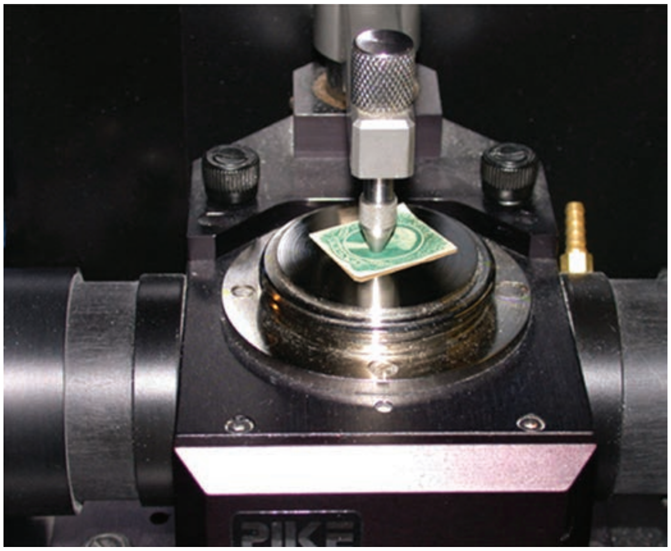

FIGURE 3. View of the attenuated total reflectance sampling accessory used to obtain FTIR spectra of the portion of stamp surface directly under the pressure clamp. In the illustration, the stamp has actually been mounted upside down in order to demonstrate the small spot size studied in each measurement. Image courtesy of the author.

RESULTS AND DISCUSSION

Study of the Paper Used in Printing of the Csa-6 and Csa-7 Issues

In the first half of the nineteenth century in America, the only source of papermaking fibers was linen and cotton rags, and the production of paper from wood pulp represents a technology not widely available until after the end of the Civil War (Sutermeister, 1954: chapter 1). Collected rags were cleaned as well as could be, cut into pieces about 2–4 inches square, and then placed in kettles where they were heated with chemicals that destroyed any coloring and rendered the pieces into a state where they could be pulverized into the component fibers that consisted entirely of cellulose (Sutermeister, 1954: chapter 2).

A very similar process is used today to produce a substance known as microcrystalline cellulose (MCC), which has found extensive use as an inactive *ingredient in pharmaceutical tablet formulations (Rowe et al., 2009:129–113). To make MCC, one starts with purified cotton and treats it with dilute solutions of mineral acids. The intermediate product is purified and filtered and eventually processed into a dry powdered form. The nature and structure of microcrystalline cellulose has been studied at length, and it has been found that FTIR spectroscopic methods are well suited for the differentiation of cellulose derivatives (Langkilde and Svantesson, 1995). As part of the present work, it has been found that microcrystalline cellulose is an excellent model compound upon which a variety of characterization studies can be based.

Figure 4 contrasts the FTIR absorption spectrum of microcrystalline cellulose with the corresponding spectra obtained from the margins of the reference stamps, and Figure 5 contains the X-ray diffraction patterns of the same regions of the same stamps. It is immediately clear from the nearly identical nature of the stacked FTIR spectra of Figure 4 that FTIR spectroscopy cannot be used to differentiate between London and Richmond paper. However, Figure 5 demonstrates that XRD analysis can differentiate between London and Richmond paper, since the XRD of Richmond paper (CSA-7R) contains contributions from crystalline components that the London paper (CSA-7L) does not contain. In fact, the paper used by De La Rue consists of the same solid-state form of cellulose as does microcrystalline cellulose.

In order to identify the crystalline component of the Richmond paper, a number of materials were wet slurried into microcrystalline cellulose, the products were allowed to air-dry, and then they were subjected to XRD analysis. As shown in Figure 6, the entire crystalline response in the XRD of Richmond paper can be attributed to the presence of kaolin (a commonly encountered form of clay) as a filler/sizer in the locally sourced paper. It

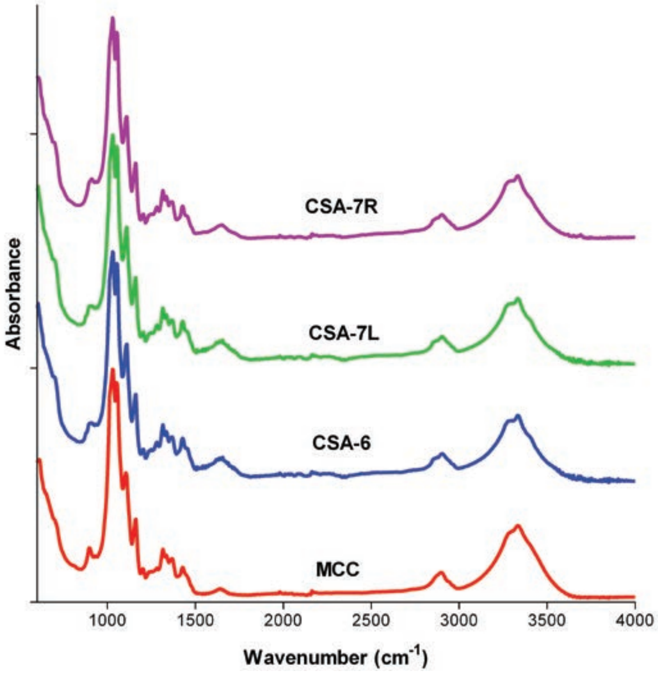

FIGURE 4. Infrared absorption spectra of microcrystalline cellulose and the corresponding FTIR spectra obtained on the margins of the reference stamps. Image used with the permission of *The Confederate Philatelist*.

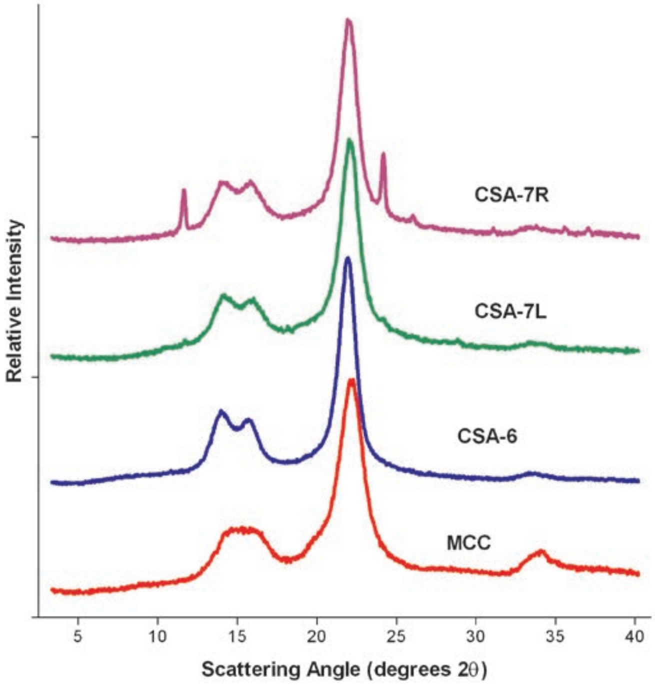

FIGURE 5. X-ray diffraction patterns of microcrystalline cellulose and the corresponding patterns obtained on the margins of the reference stamps Image used with the permission of *The Confederate Philatelist*.

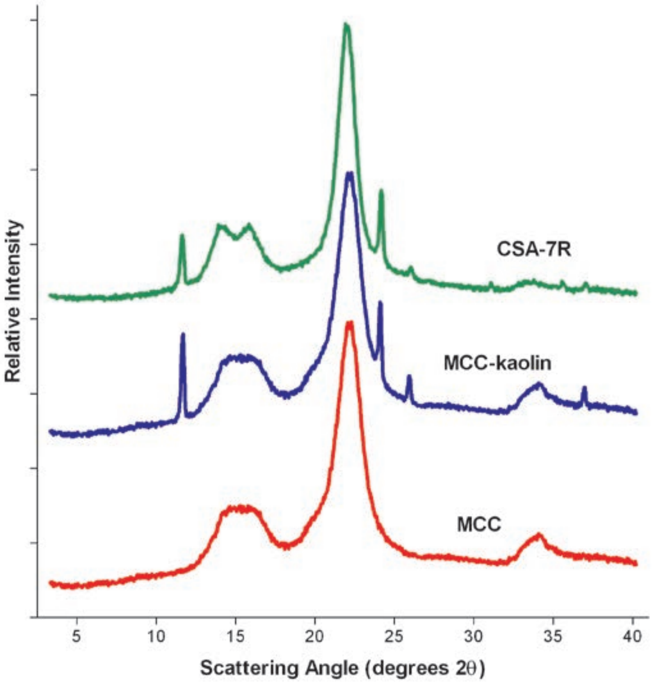

FIGURE 6. X-ray diffraction patterns of microcrystalline cellulose, a 3:7 mixture of MCC and kaolin, and the CSA-7R paper. Image used with the permission of *The Confederate Philatelist*.

is concluded from this study that the locally sourced paper used in the Richmond printings contained kaolin clay as the filler/sizer agent.

Therefore, the presence or absence of the kaolin component in the X-ray diffraction pattern of a typographed 5¢ blue Jefferson Davis stamp can be used to determine whether the paper used in the printing was sourced from De La Rue in England or whether it came from a local source in Richmond.

Studies of the CSA-6 and CSA-7 Stamp Surfaces

Before the results of studies conducted on the CSA-6 and CSA-7 reference stamps can be discussed, it is first appropriate to briefly provide some of the general characteristics of the ink used for typographic printing (Ellis, 1940). Typography consists of printing from raised characters or plates, where the paper is pressed against a printing form that consists of the image cast in positive relief. For job press printing, the paper to be printed is obtained as single sheets, and the image is created by pressing the entire sheet against the form at the same time. The plates used for typography are produced from an engraved plate, in which an image is etched onto a copper sheet using a chemical process. Since the duplicate plates can be manufactured at will from the original engraved plate, their use is preferred for extensive printing runs.

Typographic inks must be matched to the paper on which the printing is to be conducted or else the quality of the image will suffer. When printing with hard-faced paper, the printer will need to use more pressure to ensure good transfer of the image but not so much pressure that the ink squeezes out of the printing form. Suitable inks should possess as heavy a body as the paper stock will permit and should be almost buttery in nature to achieve satisfactory distribution over the plate.

In typical ink production, the pigments are first ground in oil or varnish; this mixture is then ground into a vehicle; and finally, the mixture is diluted in a medium that facilitates the workability of the ink. Because the typographic inks used in the Civil War era were oil based, their drying was not instantaneous and the vehicles used were chosen to make the drying process most efficient. European vehicles mainly consisted of mixtures of linseed oil and rosin, and the English practice was also to admix some whale oil into the vehicle for economic reasons (Ellis, 1940:197–199).

The drying process that causes the oil-based inks used in typographic printing to dry entails oxidation of the unsaturated groups in the oils, resulting in polymerization reactions that yield a dried ink film that adheres to the paper (Ellis, 1940: 224–226). In general, typographic inks undergo minimal chemical reaction with the paper on which they are printed.

Figure 7 contrasts the X-ray diffraction patterns of microcrystalline cellulose along with the corresponding diffraction patterns obtained from the faces of the reference stamps. It is

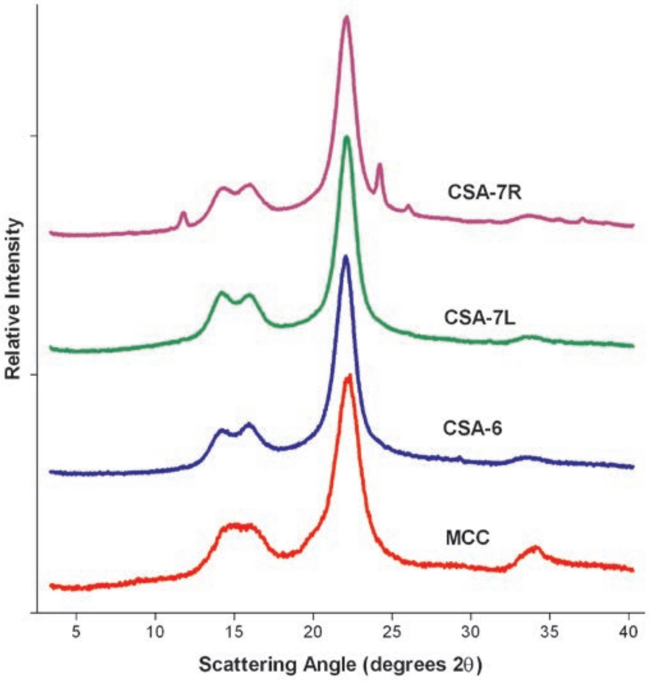

FIGURE 7. X-ray diffraction patterns of microcrystalline cellulose and the corresponding patterns obtained on the faces of the reference stamps Image used with the permission of *The Confederate Philatelist*.

immediately obvious from a comparison of Figures 5 and 7 that the XRD pattern of the stamps is completely determined by the composition of the paper and that the XRD patterns do not contain any contribution from the printing ink. This finding confirms that XRD analysis can be used to distinguish between Richmond prints on London paper and Richmond prints on Richmond paper. However, it is equally clear that XRD analysis cannot be used to distinguish between CSA-6 stamps and CSA-7 stamps printed on De La Rue paper.

Figure 8 contains the infrared absorption spectra of microcrystalline cellulose along with the corresponding absorption spectra obtained from the faces of the reference stamps. Examination of the figure reveals a number of differences between the spectra of the CSA-6 and the CSA-7 stamps as well as a high degree of similarity between the spectra of the CSA-7L and CSA-7R stamps. For reasons that will become apparent in the following discussion, the spectral differences can be classed into three contributions, which have been marked in the figure.

Feature I of Figure 8 consists of a single absorption band, characterized by an absorption maximum of approximately 2,090 cm^{-1}. The energy of this band enables its assignment as being due to the symmetric stretching mode of a cyanide group, which leads to the conclusion that the ink of the CSA-6, CSA-7L, and CSA-7R stamps contained Prussian blue. This compound has a chemical formula that can be written as $FeK[Fe(CN)_6]$ and exhibits an intense blue color. To illustrate the identification, Figure 9 contains the FTIR spectrum of Prussian blue adsorbed onto microcrystalline cellulose, along with the FTIR spectra of the CSA-6 and CSA-7L reference stamps.

Feature II of Figure 8 actually consists of two absorption bands, a sharp band at approximately 665 cm^{-1} and a much broader band at approximately 1,000 cm^{-1}. These absorption bands are associated with the presence of a single species, which has been identified as talc. As evident in Figure 10, the broad talc absorption band has a significant overlap with the main cellulose absorption but is evident in the spectra as a shoulder on the low-energy side of the cellulose absorption.

At this point in the analysis, several conclusions can be deduced from the data presented thus far. The printing ink used for the CSA-6 stamps and for both CSA-7 issues consists of a mixture of Prussian blue (acting as the blue pigment) and talc (acting as the white pigment). It is clear that the actual color of a given stamp must depend on the relative amounts of blue and white pigment used to prepare the ink, and thus one may obtain a variety of shades of blue in stamps that contain varying proportions

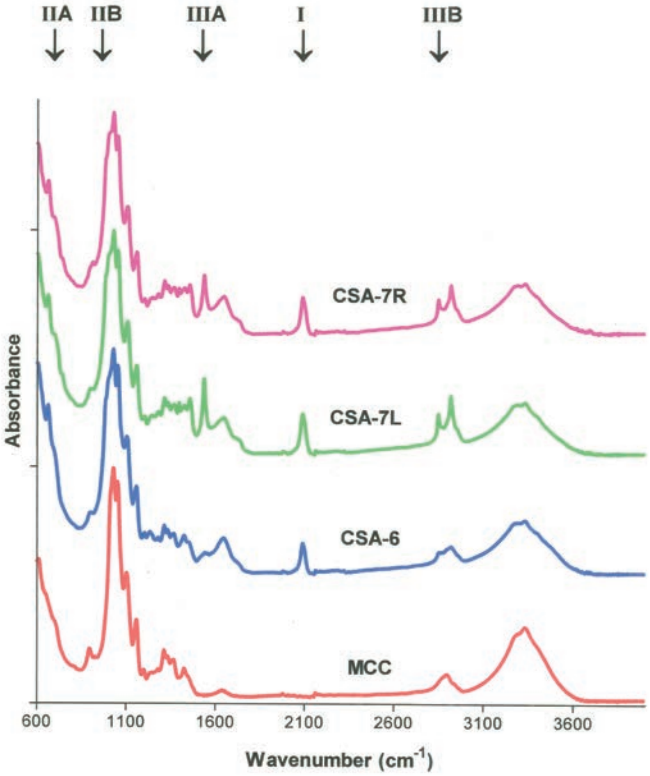

FIGURE 8. Infrared absorption spectra of microcrystalline cellulose and the corresponding FTIR spectra obtained on the faces of the reference stamps with the key analytic regions marked. Image used with the permission of *The Confederate Philatelist*.

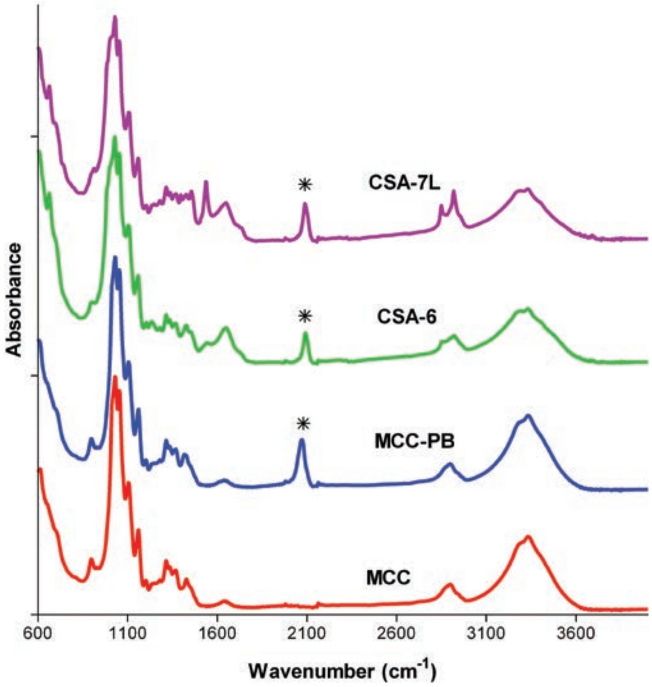

FIGURE 9. Infrared absorption spectra of microcrystalline cellulose, Prussian blue absorbed onto MCC, and the FTIR spectra obtained on the faces of the CSA-6 and CSA-7L reference stamps. The position of the Prussian blue peak has been marked, and it corresponds to feature I of Figure 8. Image used with the permission of *The Confederate Philatelist*.

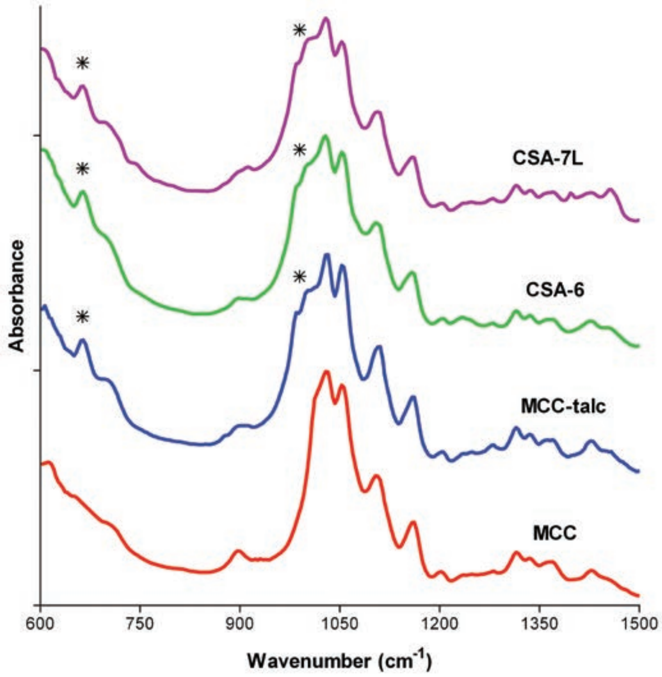

FIGURE 10. Expanded infrared absorption spectra of microcrystalline cellulose, MCC containing talc, and the FTIR spectra obtained on the faces of the CSA-6 and CSA-7L reference stamps. The positions of the talc peaks have been marked, and these correspond to features IIA and IIB of Figure 8. Image used with the permission of *The Confederate Philatelist*.

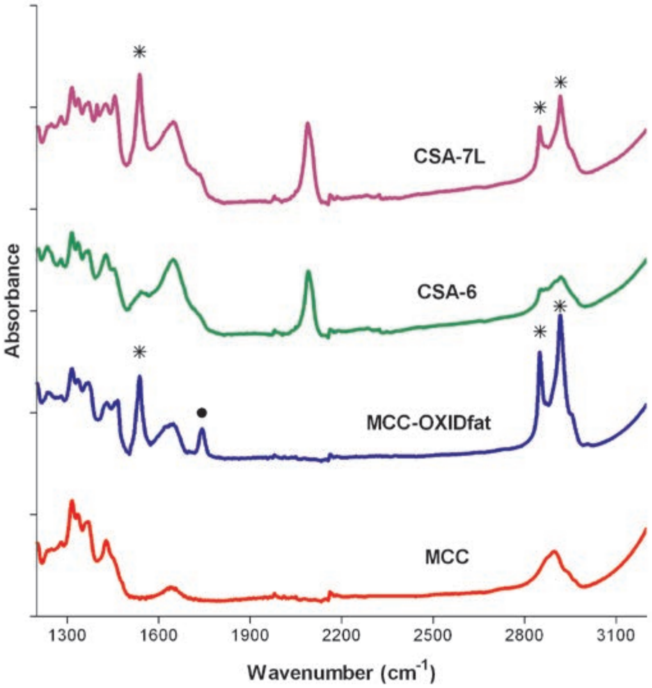

FIGURE 11. Expanded infrared absorption spectra of microcrystalline cellulose, MCC containing oxidized beef fat, and the FTIR spectra obtained from the faces of the CSA-6 and CSA-7L reference stamps. The positions of the talc peaks have been marked, and these correspond to features IIIA and IIIB of Figure 8. The feature in the MCC-OXID fat trace marked by the filled circle is due to residual unoxidized fat. Image used with the permission of *The Confederate Philatelist*.

of the two pigments. However, the pigment composition of the ink cannot be used to distinguish between London prints and Richmond prints.

Since typographic inks require the use of an oil phase as the vehicle, a number of vegetable oils were ground into microcrystalline cellulose, and the resulting mixture was subsequently oxidized with hydrogen peroxide. While these preparations could account for the hydrocarbon absorbance bands of feature IIIB of Figure 8, it was not possible to obtain the absorption bands of feature IIIA. However, oxidized proteins do exhibit absorption bands in this region, and therefore, preparations were made in which animal fat (commercial lard and beef fat) was ground into microcrystalline cellulose, and the mixtures were oxidized with hydrogen peroxide. As shown in Figure 11, the inclusion of oxidized oily animal fats in microcrystalline cellulose was successful in reproducing the absorption bands of features IIIA (1,535 cm^{-1}) and IIIB (2,580 and 2,515 cm^{-1}).

It is concluded that the printing ink used for both types of CSA-7 stamps contained a significant amount of oxidized animal fat, and the nonvolatile part of this oily fat still remains in the stamps. The oil used in mixing the ink that was used in the printing of the CSA-6 stamps must have been much more volatile than the fat/oil used for the Richmond prints, as there was very little residual nonvolatile component evident in the FTIR spectra of these stamps. Given the practice at the time, it is most probable that this oil was derived from a vegetable origin and was probably linseed oil. The studies have demonstrated that FTIR spectroscopy can be used to distinguish between London prints and Richmond prints on the basis of the residual oil/fat remaining in the printing ink.

The results of the FTIR analysis of the inks used in the various printings of the typographed 5¢ blue Jefferson Davis stamps are most succinctly summarized in Figure 12, where the FTIR spectra obtained from the faces of the reference stamps can be simulated by the superimposition of the FTIR spectra of microcrystalline cellulose and the identified components in the corresponding printing inks. The FTIR spectrum for a theoretical CSA-6 stamp was simulated by numerically averaging the spectra of MCC containing talc and MCC containing Prussian blue, while the spectrum for a theoretical CSA-7 stamp was simulated by averaging the spectra of MCC containing talc, MCC containing Prussian blue, and MCC containing oxidized beef fat.

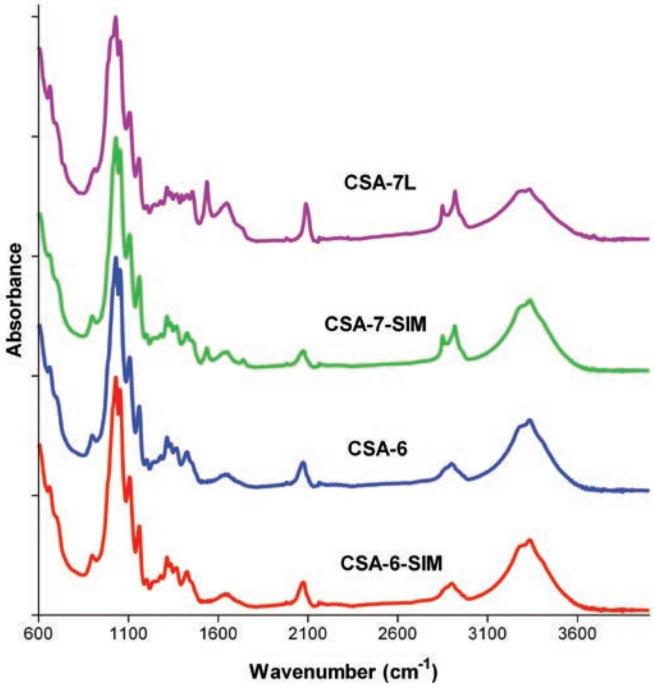

FIGURE 12. Infrared absorption spectrum simulated for a theoretical CSA-6 stamp (obtained by averaging the spectra of MCC containing talc and MCC containing Prussian blue) and the spectrum simulated for a theoretical CSA-7 stamp (obtained by averaging the spectra of MCC containing talc, MCC containing Prussian blue, and MCC containing oxidized beef fat). Also shown are the FTIR spectra obtained on the faces of the CSA-6 and CSA-7L reference stamps.

CONCLUSIONS

The forensic analysis of typographed 5¢ blue Jefferson Davis stamps that were issued by the Confederate States of America has revealed a number of distinctive features that enable one to differentiate among the various subtypes. The analytical process requires a measurement of both the X-ray diffraction pattern and the infrared absorption spectrum of a given stamp in order to make the correct identification.

The first printings of the stamps (CSA-6) were made in London by the De La Rue Company and were made using ink and paper that was sourced in London. Collectors have usually recognized these stamps by the superior quality of their images, which undoubtedly came about by good matching of paper and ink by De La Rue. Using the forensic tools described in this paper, an analyst can identify these stamps on the basis of their XRD pattern (which contains features due to cellulose only, with no peaks associated with the presence of kaolin) and their FTIR spectra (indicative of Prussian blue and talc pigments but essentially lacking a contribution from residual oil).

The initial stamps printed in Richmond by the Archer & Daly Company (CSA-7 L) were made using ink that had been mixed locally on paper provided by De La Rue. The images on these stamps are not as good as the images of stamps printed in London by De La Rue, and this represents the lower-quality matching of ink and paper. The analyst can identify these stamps by means of their XRD pattern (which contains features due to cellulose only, without peaks associated with the presence of kaolin) and their FTIR spectra (indicative of Prussian blue and talc pigments but now exhibiting a significant contribution from residues associated with oxidized animal oil or fat).

When the supply of London-sourced paper was exhausted, additional printings of 5¢ blue Jefferson Davis stamps (CSA-7R) were made using the same locally mixed ink and locally sourced paper. These stamps usually feature the lowest-quality images, which are associated with poor matching of ink and paper. These stamps are identifiable on the basis of their XRD pattern (which contains features due to cellulose and significant peaks due to the presence of kaolin in the paper) and their FTIR spectra (indicative of Prussian blue and talc pigments and exhibiting a significant contribution from residues associated with oxidized animal oil or fat). For additional information on this issue please see Brittain (2013).

ACKNOWLEDGMENTS

I thank Jerry Palazolo for his loan of the CSA-6 reference block used in this work. Special thanks are also due to Thomas Lera and Patricia A. Kaufmann for their encouragement, review, and support of the approach I have taken for the forensic analysis of Confederate stamps.

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Forensic Analysis of Great Britain 1858–1879 1d Plate 77 Stamps on Cover

Abed H. Najjar

ABSTRACT. In 2003, the author obtained an 1865 cover franked with three Great Britain 1858–1879 1d plate 77 stamps (SG 43). If genuine, this is a very valuable and historically significant philatelic item. Discoveries of plate 77 stamps are always met with suspicion because they are so rare and have often been the subject of attempted fakery. This paper presents a detailed scientific study of this cover and the stamps. It begins by presenting a compilation of possible methods that might be used for faking the plate 77 stamps. It then develops an analysis plan that carefully examines each possibility. Appropriate analytical equipment is identified for each step in the process. Finally, the stamps in question are subjected to rigorous testing. The majority of the testing was performed by state-of-the-art, independent laboratories in the United Kingdom and the United States. Many different analyses were employed. These included optical and scanning electron microscopy, X-ray fluorescence spectroscopy, Raman spectroscopy, and more. The paper then presents the results of these analyses and the conclusions drawn from them. All of these data were reviewed by outside forensic experts in order to validate the scientific procedures. Two anomalies that arose during testing are discussed, and hypotheses are posed to account for them.

INTRODUCTION

An 1865 part cover (Figure 1), which was sent from Guernsey to Brussels, was written in the hand of the famed literary figure and playwright Victor Hugo, who resided at Hauteville House in Guernsey. Hugo lived on the island between 1855 and 1870. The letter, which was dated 27 November 1865, is addressed to his publishers La Croix Verboeckhoven in Brussels. This fact was confirmed by Mr. Adrien Legendre, specialist in books and manuscripts, Sotheby's Paris, who confirmed as follows: "In my opinion, the handwriting on the envelope is Victor Hugo's."[1] This cover will henceforth be referred to as the Victor Hugo cover.

The cover, sent from Guernsey to Hugo's publishers in Brussels, was franked with three examples of the iconic Great Britain 1858–1879 1d stamp showing a plate number 77. The stamps were canceled with the Guernsey 324 duplex dated 27 November 1865. The cover also carried a "PD" mark in red and was hand stamped with the ANGLETERE/AMB. OUEST2- TPO mark and the BRUXEL arrival circular date stamp of 28 NO 65.

Because only a handful of accepted examples of this iconic stamp are known to exist, it is understandable the discovery of three used examples of this rarity on a part cover would be treated with much skepticism by the philatelic world. The purpose of this paper is to describe the analytical methods used to determine whether these stamps are genuine.

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FIGURE 1. Victor Hugo cover.

The accepted and provenanced stamps showing a plate number 77 have always been considered by the philatelic world to have been printed from plate 77. There was never a reason to question this fact, and with so few examples known there was never a need to research them.

Illustrated in Figure 2 are images of two of the accepted plate 77 stamps. These are the unused stamp BA (indicated by the letters next to the words "ONE PENNY"), now in the Tapling collection, and the used example stamp PH, the Fletcher copy, both in the philatelic collection at the British Library.[2]

The discovery of the 1865 Victor Hugo cover franked with three examples showing a plate number 77 has shed a completely new light onto the origin of these rare and iconic stamps from Great Britain. Comparing the position of the corner letters of the three stamps and the presence of a major plate flaw confirms these three stamps originated from plate 73.

FIGURE 2. Left: Great Britain 1858–1879 1d red plate 77, BA, unused, the Tapling Collection, Great Britain section, page 28. Right: plate 77, PH, used, the Fletcher Collection, volume 81, page 2. Courtesy of the British Library Philatelic Collection.

The image in Figure 3 is that of the imprimatur stamps from plate 73. The stamps in Figure 4 are from the Victor Hugo cover.[3] The arrow indicates the distinct flaw under the letter "S" in the top right box on stamp SK. This flaw is mirrored on stamp SK (Figure 4) from the Victor Hugo cover, which shows a plate number "77," and the corner letters are identical in their positions on both stamps.

These features undoubtedly indicate that the printers, Perkins, Bacon & Co., must have reengraved some impressions on plate 73 with the plate number "77" clearly before 27 November 1865, the date the three stamps were canceled, and in view of the great rarity of this trio must have then corrected them back *very soon* afterward using the plate 73 transfer roller to their original plate number 73. Plate 73 continued to print stamps until early 1868, printing a total of 529,900 sheets.

FIGURE 3. Plate 73 imprimatur stamps SK and SL. ©The British Postal Museum and Archive, 2012.

FIGURE 4. Stamps SK and SL from the Victor Hugo cover.

The discovery of this remarkable cover, which is franked with three stamps that undoubtedly show interesting philatelic anomalies, necessitated in-depth research into all the accepted plate 77 stamps.

For the purpose of this discussion, this paper will be divided into two sections: first, a comprehensive scientific investigation to rule out the possibility of faking or counterfeiting these three stamps and second, research into plate 77 and the accepted stamps showing a plate number 77 with discussion on why and how the reengraving was carried out and the possible reasons for producing "plate 77" stamps in this way.

THE COMPREHENSIVE SCIENTIFIC INVESTIGATIONS

What is in question is the following: have three stamps been manipulated and altered in five different locations to the extent of altering five printed figure "3"s into five faked figure "7"s; have the paper fibers in these five small areas been disturbed, moved, or altered; and has any foreign ink been used in order to carry out this faking process?

Having examined these stamps the moment they were discovered using a light microscope at ×100 magnification and a UV light, no evidence whatsoever has been found of any faking, fiber disturbance, evidence of painting, or any other attribute that would indicate that these stamps have been manipulated.

In order to obtain an endorsement from the expert philatelic bodies, the stamps were first presented to the Royal Philatelic Society London (RPSL)[4] and then to the Philatelic Foundation of New York (PF)[5] for an expert opinion (Figure 5).

The RPSL Expert Committee issued a certificate of opinion, number 194446 dated 13 September 2006, which stated "stamps are not from plate 77 but have been faked in each case using a stamp from plate 73." On 3 October 2006, the RPSL reiterated its opinion by stating the plate 73 numbers had been modified into 77s through a "cut and paste" method.

The PF Expert Committee issued certificate number 457736 dated 6 November 2007, which stated "The stamps are not from plate 77, rather the second digit of each stamp has been altered to resemble a 7." The PF expert responsible for this opinion believes this was done through "abrading to un-inked paper and painting." The certificate is hand-stamped in red with the words "ALTERED OR COUNTERFEIT."

These two opinions, which allege that the stamps had been faked, necessitated scientific analysis, the only route by which one can establish their validity.

It is worth mentioning that the alleged alteration would have to have been carried out five times on the five visible 7s on three stamps, on most of which the cancel falls over the second "7." This faking would need to have been done on an area that does not exceed 2 mm in width, with the downstroke of the number 7 measuring 0.6–0.8 mm (Figures 6 and 7). This is a very small area indeed for such complicated faking work to be carried out.

In order to establish the stamps have not been tampered with, the Victor Hugo cover and the three "plate 77" stamps were subjected to a wide variety of scientific examinations by renowned organizations that used state-of-the-art scientific equipment. The services of two independent forensic scientists, Mr. Robert Radley, who specializes in the field of document tampering, and Professor Alan Jamieson, both of the Forensic Institute,[6] were also employed.

The following possible methods of alteration were investigated:

Removing stamp design elements:

- inlaying (i.e., cut and paste),
- scraping,
- powder blasting or laser obliteration, and
- chemical erasure, partial or complete.

Adding stamp design elements:

- retouching small areas and
- retouching the whole "diamond."

Table 1 summarizes the various possible methods by which the stamps could have been altered and the various scientific examinations that were used in order to determine their validity.

THE SCIENTIFIC METHODS USED TO ESTABLISH NONTAMPERING

SCANNING ELECTRON MICROSCOPY SURFACE ANALYSIS OF THE PAPER FIBERS

Scanning electron microscopy (SEM) is a form of microscopy that allows for the large magnification of an area, providing an almost three-dimensional image, making the analysis of

The Philatelic Foundation
70 West 40th Street • 15th Floor
New York, NY 10018
EXPERT COMMITTEE

No. 457736
11/06/2007

WARNING
IN OUR OPINION
THIS ITEM IS ALTERED OR COUNTERFEIT
READ YOUR CERTIFICATE CAREFULLY

We have examined the enclosed item, of which a photograph is attached, and *described by the applicant* as follows:

Country: GREAT BRITAIN

Cat. No.	Issue	Denom.	Color
33	1864	1p	rose red

Scott's unless otherwise specified.

THREE 1p, ALL PLATE 77, SINGLE & VERTICAL PAIR, ON OPENED OUT COVER ADDRESSED TO BELGIUM 1865 GUERNSEY DUPLEX CANCEL WITH TWO NUMERAL "324" BARRED OVAL CANCELS, BRUSSELS 28 NOV 65 RECEIVING BACKSTAMP.

AND WE ARE OF THE OPINION THAT:

THE STAMPS ARE NOT FROM PLATE NO. 77, RATHER THE SECOND DIGIT OF EACH STAMP HAS BEEN ALTERED TO RESEMBLE A "7". ***************

457736

F 178466

For The Expert Committee
Chairman

Photocopies of this Certificate are not valid.

Submitted by ABED H. NAJJAR

No. 194468
THE ROYAL PHILATELIC SOCIETY
LONDON

41 Devonshire Place
London W1G 6JY

Meeting of 13 SEP 2006

In the OPINION of The **EXPERT COMMITTEE** the item described as
Great Britain 1864 S.G. No. G1
1d Rose-red – Perf 14 – Plate 77 – Three used on part cover to Brussels – are not from Plate 77 but have been faked in each case using a stamp from Plate 73.

Chairman

Submitted by Abed H Najjar

FIGURE 5. The PF and RPSL certificates.

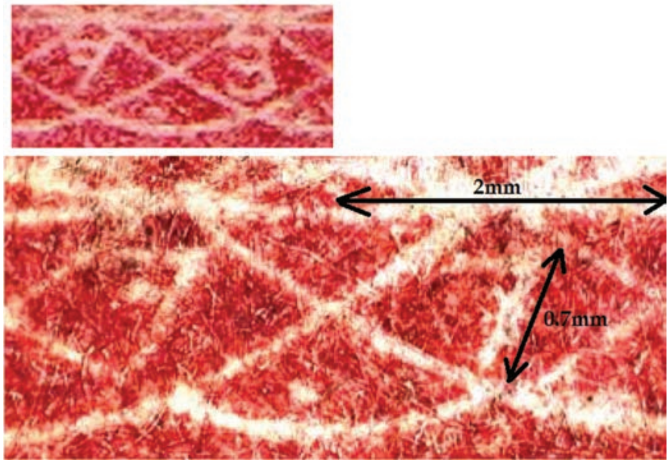


FIGURE 6. Images of (top) the figure 73 from a plate 73 stamp and (bottom) the figure 77 from stamp SK on the Victor Hugo cover.

an image a much easier task. SEM uses an electron beam to trace over the surface of an object, dislodging electrons from the surface, which are in turn attracted by a secondary electron detector. This produces an image by registering different levels of brightness on a monitor.

SEM provided by Reading Scientific Services Ltd. (RSSL)[7] was used to study the surface of the right-hand "7"s to see if there were any fiber disruption or the addition of foreign paper fibers, and as can be seen in Figure 8, the surface is completely untouched.

The two SEM images in Figure 8 are from stamp SL on the Victor Hugo cover. These clearly show the paper fibers are matted together and completely intact and undisturbed.

The SEM image in Figure 9 is the left-hand "77" on stamp SK, shown in backscattered mode. The heavy elements forming the printing ink show up brightly within the diamond. It is important to note that both "7"s show similar "dark" features. If the right-hand figure "7" originated from a cleaned or a bleached figure "3," then the figure "7" would not have been as clear and

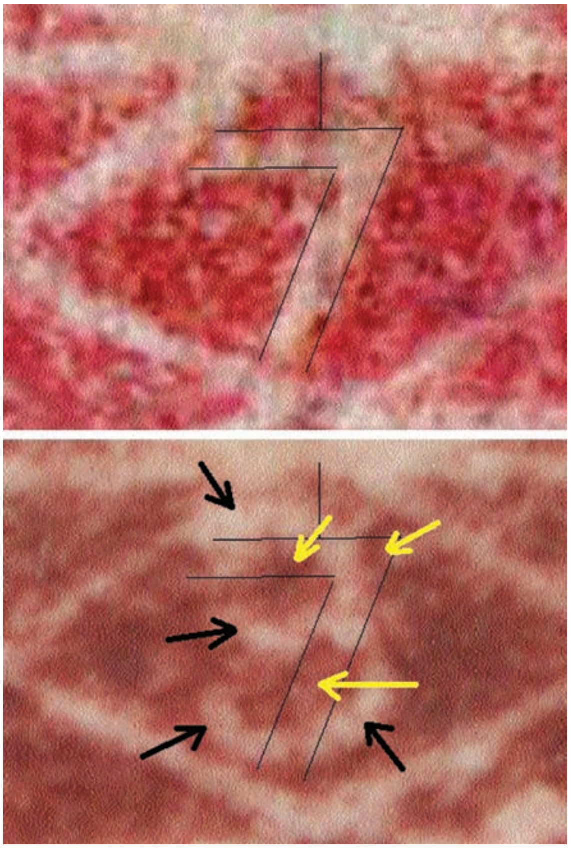


FIGURE 7. Image of the figure “3” from a plate “73” stamp and the figure “7” from stamp SK on the cover. A black outline has been drawn around the “7” and superimposed in the same location in the figure “3” diamond in order to show which areas need alteration and painting. It is clearly evident that the whole area needs to be completely altered in color, with some red areas needing to become “colorless” indicated by the yellow arrows and others needing to become “red” indicated by the black arrows.

definitive as it appears as existing elements from the ink would still be present. Furthermore, there is no indication of any previous number being present.

If the figure “7” had been derived from a figure “3” as shown on the left, then the areas marked with arrows on the SEM image would appear as bright spots where the ink from the figure “3” would have been.

Figure 10 shows two photomicrographs of the right-hand figure “7” from the right panel from stamp SK. The image on the left was taken by Professor Gene Hall at Rutgers University, and that on the right was taken by the RSSL. The identical features of the left-hand “7”s can be seen between both images. It is also interesting to note that the small area of disturbed fibers in the center of the diagonal of the figure “7” clearly illustrates the fact that had the area been disturbed in order to alter the number, then such a feature would be prevalent throughout the diamond area.

X-Ray Microfluorescence

X-ray microfluorescence (EDXRF) is a nondestructive method for detecting and analyzing the elements in inorganic substances. The XRF spectrometer measures the individual component energies of the X-rays emitted when the sample is irradiated with an X-ray beam. A spectrum is produced that depicts those elements found in a specific area.

EDXRF was used by both Professor Gene Hall and the RSSL in order to analyze the elemental components of the ink used to print the stamps. Both the right-hand and left-hand “7”s were analyzed in order to look for similarities or differences together with a normal plate 73 stamp for comparison.

Figure 11 is a plot from an EDAX International (Mahwah, N.J.) micro EDXRF Eagle II spectrometer used by Professor Gene Hall. EDXRF revealed the diamond inked area around the second “7” in plate number “77” contained the same elements (Hg, S, Pb, Ca, K, Al, and Si) as in the diamond inked area around the first “7” with additional elements of barium (Ba) and

TABLE 1. Analytical methods evaluated.

	Analytical method						
	Microscopy		Near-visible light		Spectroscopy		Profilometry (digital microscopy)
Modification type	**Optical**	**Scanning electron**	**Ultraviolet**	**Infrared**	**EDXRF**	**Raman**	
Inlaying	✓	✓	✓		✓		✓
Scraping	✓	✓					✓
Powder blasting or laser obliteration	✓	✓					✓
Chemical erasure			✓	✓	✓	✓	✓
Retouching small areas	✓	✓	✓	✓	✓	✓	✓
Retouching the entire diamond	✓	✓			✓	✓	✓

FIGURE 8. SEM images of the paper fibers of stamp RL from the Victor Hugo cover.

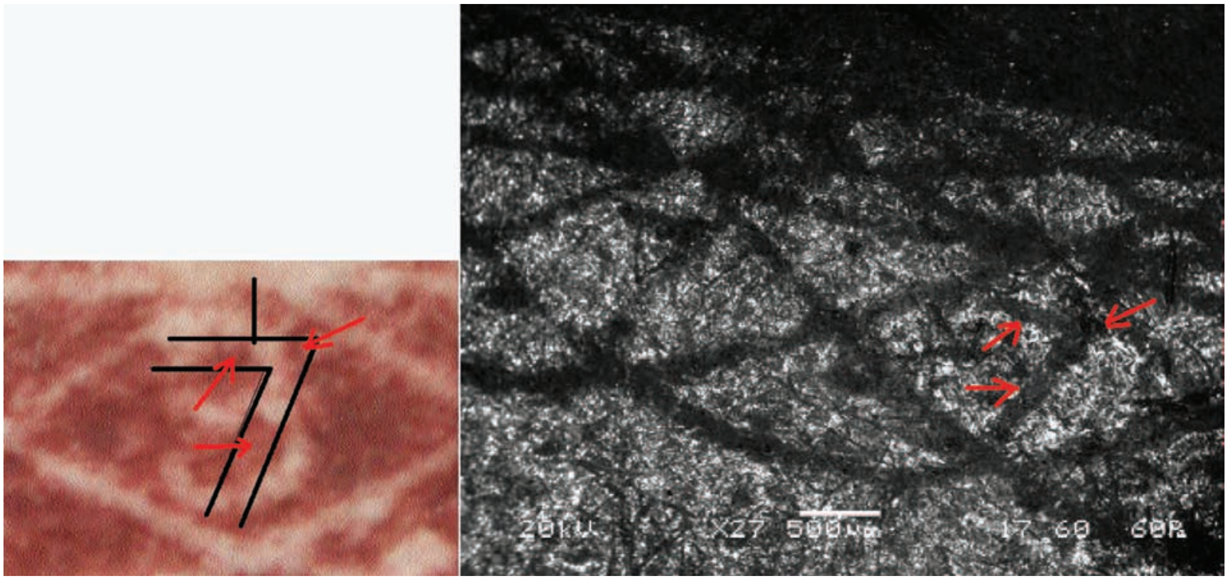


FIGURE 9. Right: Backscattered SEM image of stamp SK from the Victor Hugo cover. Note that all the uninked colorless areas appear dark on the image. Left: The red arrows indicate the area where the existing red ink must be altered/removed in order to produce a colorless figure "7" from the existing figure "3."

chromium (Cr) in a spot location and was not homogenously distributed around this diamond inked area. The elements Ba and Cr were not found in the diamond area around the first "7" in the plate numbers "77" and "73" examined.

Both "7"s showed that identical elements were used for the printing ink. In addition, the right-hand "7" showed extra trace elements of chromium, barium, and phosphorus, which can only be regarded as plate contaminants originating from the platemaking process.

RAMAN SPECTROSCOPY

Raman spectroscopy is another nondestructive method of analyzing the inorganic components in the printing ink. The

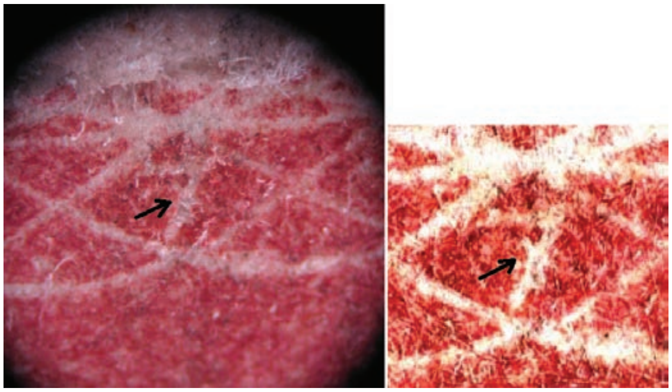


FIGURE 10. Photomicrographs of the stamp SK on the Victor Hugo cover. The black arrows indicate the area of the minute paper disturbance.

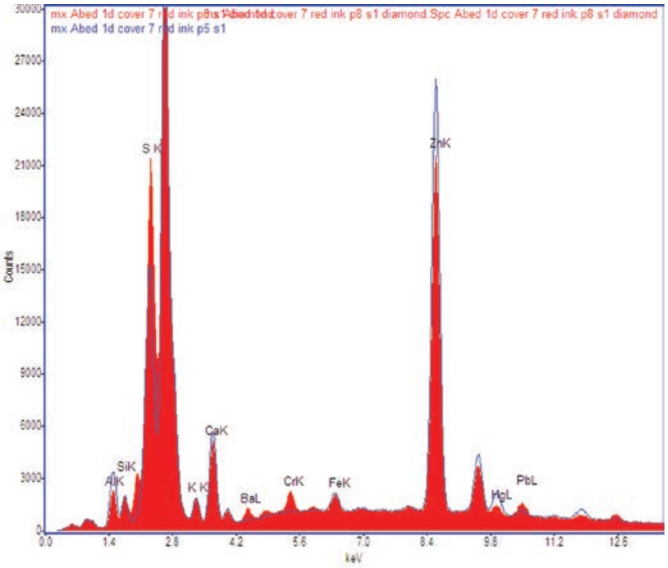


FIGURE 11. EDXRF comparison of red ink around the first (blue trace) "7" and around the second (red trace) "7" in the plate number "77." Notice the appearance of Ba and Cr in the second "7."

difference between this and EDXRF is that Raman excites molecules rather than atoms. It works by irradiating molecules using light from a laser beam. The irradiated molecules will produce Raman scattering, which is measured and identified. Raman can determine the chemical compound that these elements belong to. This is only possible if the chemical compound is in a reasonable concentration and the compound is a high Raman scatterer.

Raman spectroscopy was used by Professor Gene Hall to analyze the molecular components of the ink used to print the stamps. Both the right-hand and left-hand "7"s were examined in order to characterize similarities and/or differences.

A Renishaw (Hoffman Estates, Ill.) system 1000 Raman microscope equipped with a Leica microscope was used to analyze the chemical composition of the pigments in the printing inks used on the stamps. Raman scattering in the stamps was produced by excitation with a 785 nm diode laser. The beam size of the laser was 2 μm, using a ×50 objective lens, and the laser power at the sample surface was reduced to 15 mW to prevent any damage due to burning of the stamps. Emphasis was focused on areas around the second "7" diamond area, which showed the presence of additional elements of Ba and Cr from the EDXRF analyses.

Raman analyses revealed the red pigment in the printing ink was composed of vermilion (HgS) and red lead (Pb_2O_3). Unfortunately, the chemical compound associated with Ba that was determined by EDXRF could not be identified. Chromium, the trace element also found using EDXRF, was identified as lead chromate; this was not homogenous or part of a faking ink, according to Professor Gene Hall.

The Raman scan in Figure 12 shows the presence of lead chromate in the sample point on the second "7" from a stamp on the Victor Hugo cover. The red/orange trace shows the sample point from the stamp on the cover. The blue trace shows the Iconofile cinnabar cold and the black trace, the lead chromate (Aldrich) standard. Since the sample point has only traces of lead chromate, they show only as small, but significant, "bands" in the scan.

The band at 842 cm^{-1} of the lead chromate, which must be very strong, is particularly weak in this case, as can be seen in the trace in Figure 12, indicating that this compound is present in minute trace quantities.

The Raman plot in Figure 13 expands the right-hand side of the sample shown in Figure 12. The red/orange trace shows the standard for vermilion (HgS), while the two blue traces show the red color in a plate 73 stamp AB reference copy (upper trace) and a plate 77 stamp on the Victor Hugo cover (lower blue trace). Vermilion was used to print both reference stamp AB and the diamond area of the second "7" from the Victor Hugo cover.

PROFILOMETRY/TOPOGRAPHY

Profilometry was used to study the topography of the surface and to look at the figure "7" in three dimensions. In this way one can eliminate the possibility that faking has taken place, through paper fiber disruption and painting. Furthermore, a recessed "7," if seen, could be produced only via impact, as with a surface relief printing process. The work was carried out at the RSSL using a Keyence VHX-600E digital microscope.

The resulting images (Figures 14 and 15) are astounding. Not only can one see the right-hand figure "7" as recessed, but enlargements show that the paper fibers are totally untampered and, as can be seen from the images, run in and out of the figure "7," changing in color as they do. Furthermore, even bigger enlargements show the white fibers of the "7" totally devoid of any ink particles, colored or "bleached."

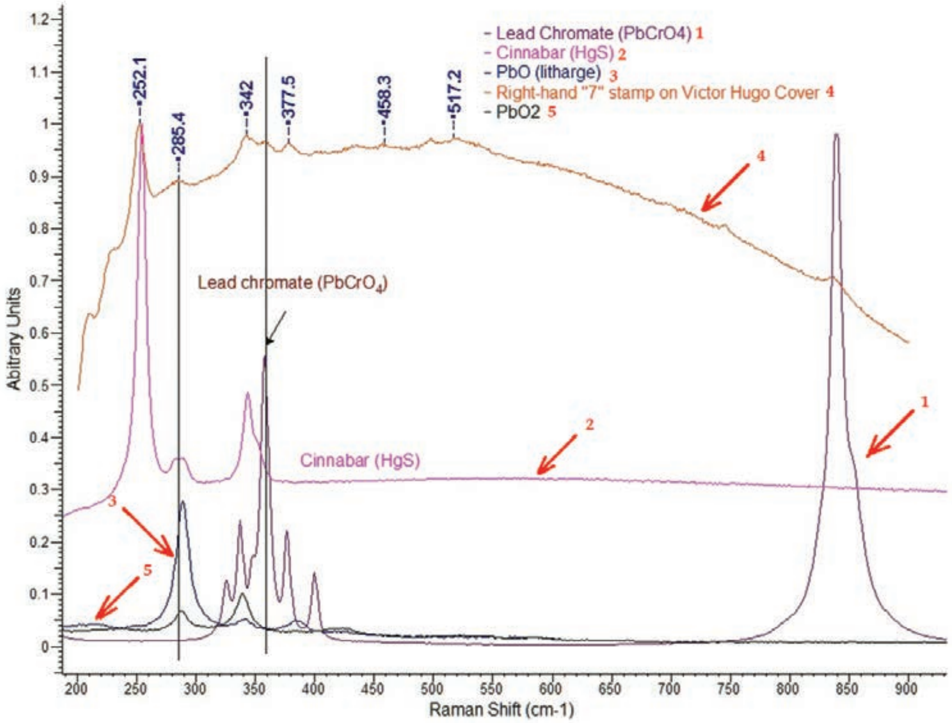


FIGURE 12. Raman spectra comparison diamond area around second "7" in plate "77."

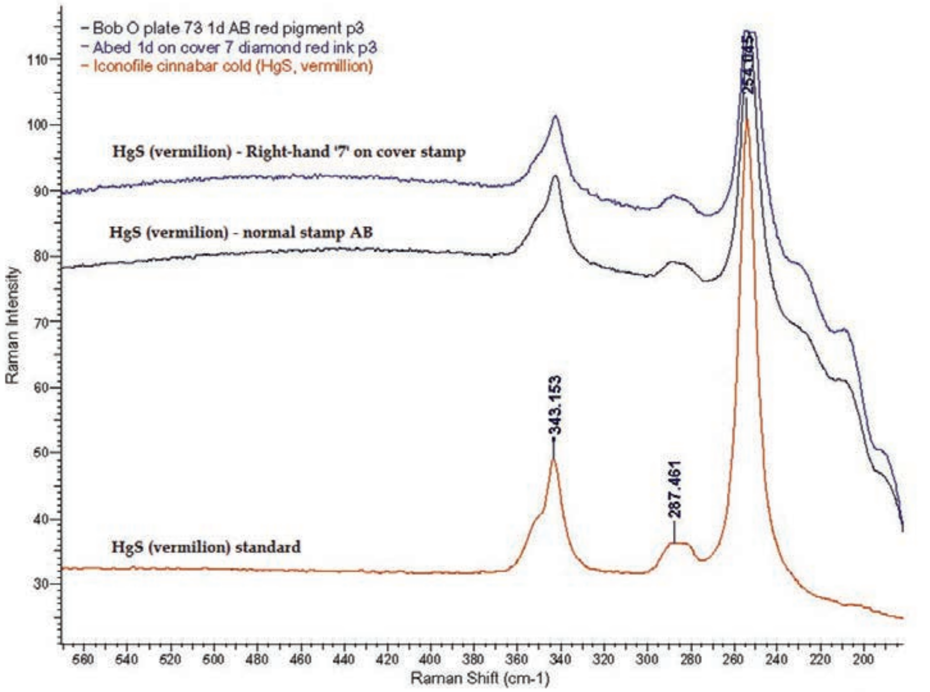


FIGURE 13. Raman spectra comparison of red ink on the diamond area around the second "7" and "3" in plate numbers "77" and "73."

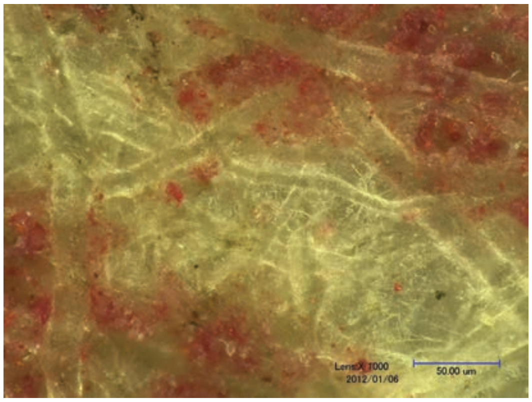
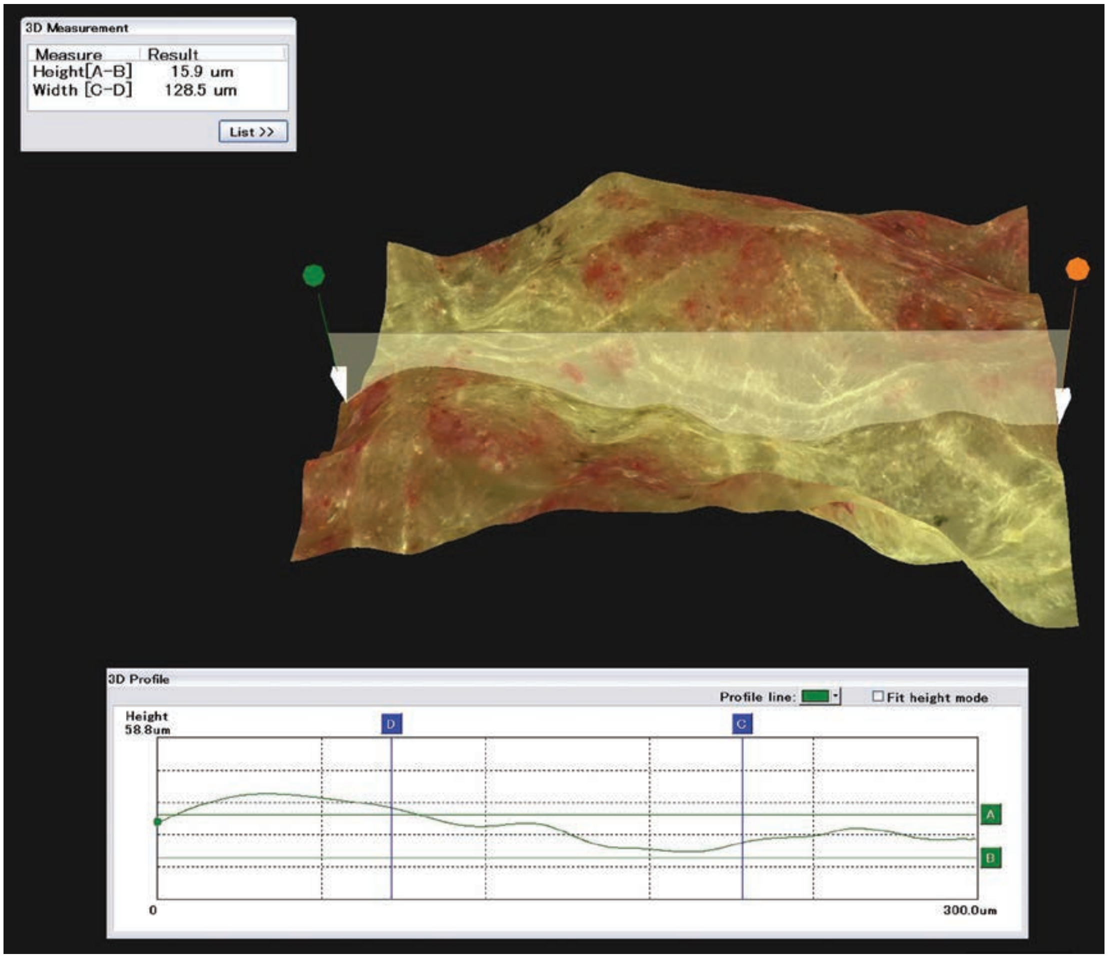


FIGURE 14. Depth composition analysis of the top of the right-hand "7" from stamp SL from the Victor Hugo cover. Such a recess of a colorless area can be produced only through impact between the plate and the paper at the time of printing and cannot be produced through faking.

Infrared Light

Infrared luminescence and reflectance can be used to show the effect of any chemical treatment. Infrared light from an IR source and from a comparator was used to observe any differences between the two "7"s. An ACO Electronics QDX-630BE-2 Questioned Document Examination System was used for these observations.

The infrared image (Figure 16) of stamps SK and SL is seen at 695 nm. The right-hand "7" in each label shows up darker than the right-hand "7." This anomaly was observed by myself, Professor Allan Jamison of the Forensic Institute, and Mr. Robert Radley of the Forensic Document Laboratory. While it certainly did not mean faking, this anomaly did require addressing and an explanation. For this observation to be deemed as faking, several other factors must also be observed in order to confirm that the stamps were faked, factors such as fiber disruption, faking inks, abrading, painting, chemical manipulation, or the insetting of paper. Clearly, even from the most basic of observations it was confirmed this did not happen.


3D Measurement

Measure	Result
Height[A-B]	15.9 um
Width [C-D]	128.5 um

FIGURE 15. Micrograph showing top section of magnified "7" on RHS of stamp SL from the Victor Hugo cover.

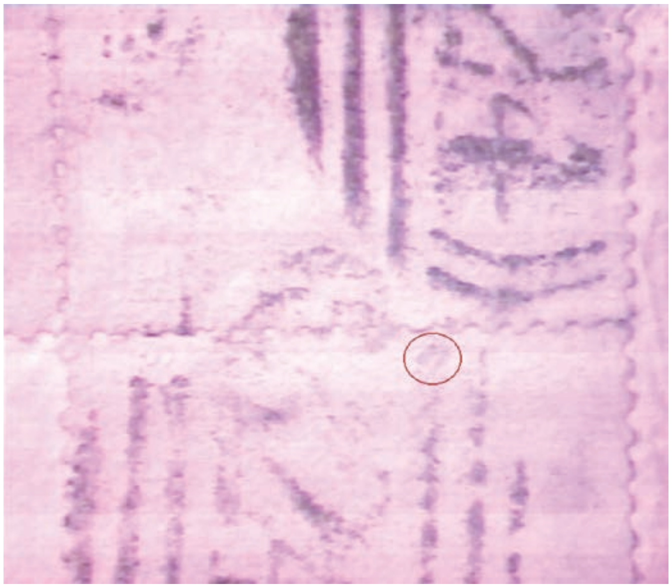


FIGURE 16. Infrared image of stamps SK and SL from the Victor Hugo cover. The right-hand figure "7" can be seen as a darkened area (circled in red).

The scientific evidence has confirmed that there was a total lack of any tampering with the paper fibers or the application of any faking ink. This must mean that the trace elements of barium and chromium must have been introduced during the reengraving process that was carried out on the plate in the right-hand diamond area on which the number was altered from a figure "3" into a figure "7." The already existing left-hand figure "7," which was not altered, does not show the presence of these trace elements.

Ultraviolet Light

High- and low-intensity ultraviolet light was also used to examine the stamps. Such a process may show if the areas under question have been chemically treated or have been retouched.

There were no differences seen between the two "7"s under UV light (Figure 17). This image was viewed at a wavelength of 365 nm using an ACO Electronics QDX-630BE-2 Questioned Document Examination System.

FIGURE 17. Ultraviolet image of stamps SK and SL from the Victor Hugo cover.

Microscopy

Optical microscopy is another useful way of examining these stamps, bearing in mind the far more elaborate methods that were used. Using light microscopy at magnifications of up to ×140, no fiber disturbance was noticed. As we can see from Figure 18, which was obtained from a printed area of stamp SK at a magnification of ×100, the paper fibers are matted and very much interwoven, and any tampering, abrasion, scraping, or removal of these fibers would undoubtedly be clearly seen under this magnification.

CONCLUSION

Conclusions of the Experts

The following conclusions, summarized in Table 2, have been extracted from the five reports obtained from the five scientific experts and expert groups who have examined the stamps first hand. It is clear they are unanimous in their conclusions.

1. Professor Gene Hall, Rutgers University[8]
   "I found no evidence to support the hypothesis that paper fibers were removed or added to the second '7 diamond region' on all three stamps. In addition, the chemistry of the inks surrounding all '7s' are identical except for differences in concentration."
2. Mr. Robert Radley, the Forensic Document Laboratory[9]
   "I find no evidence of substance to significantly support the proposition that the stamps in question have been modified by an obliteration of a numeral '3' from a 'plate 73' stamp and subsequent alteration of the '3' to a numeral '7'. The technical difficulties in modifying a 'plate 73' stamp to a 'plate 77' stamp are immense and from a detailed examination of the cover in question, I find the combined evidence is inconsistent with such a procedure having been adopted."
3. Professor Allan Jamieson, the Forensic Institute[10]
   "Therefore, in the absence of evidence to the contrary, the scientifically logical conclusion is that the stamps have not been 'faked.'"
4. Mr. Tom Ray, Microscopy Laboratory Manager, Reading Scientific Services Ltd.[11]
   "I can confirm that by using a range of microscopy techniques (i.e. stereo light microscopy and scanning electron microscopy using secondary and back-scattered imaging modes), we found no evidence in terms of fiber disruption (such as deliberate tamper by scraping, cutting or adding fibers) during topographical examination of the second '7 diamond' regions on all three stamps. In conclusion,

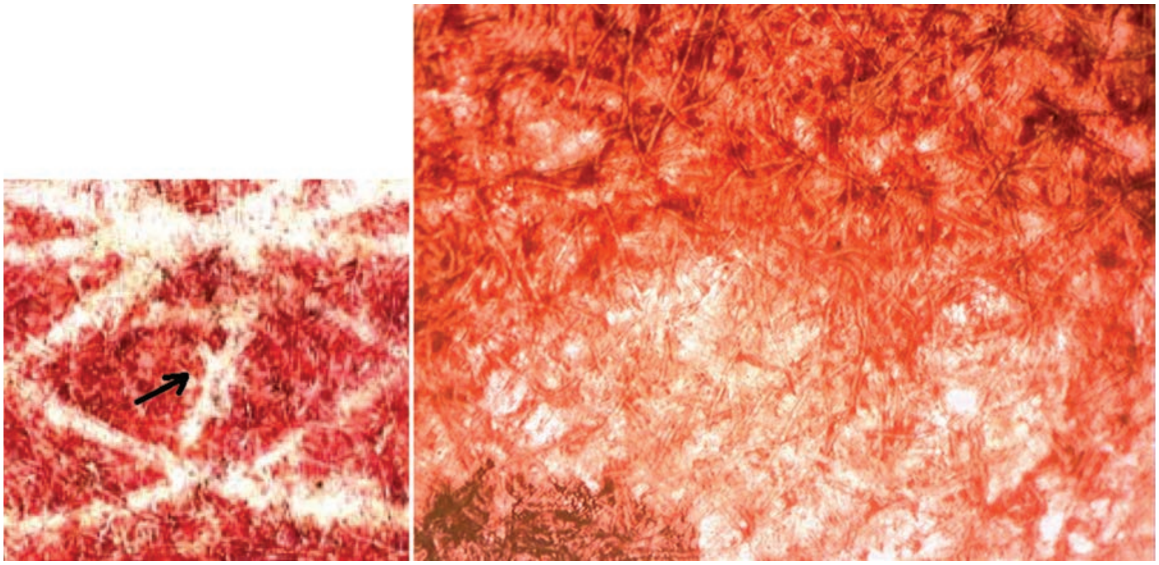


FIGURE 18. The image on the right is a ×100 enlargement of a small area (left, black arrow) from the top of the right-hand "7" of the SK stamp from the Victor Hugo cover. The general matted appearance of the paper fibers at this magnification is clearly visible, and any fiber disturbance would also be visible under this magnification.

TABLE 2. Summary of the analytical results.

	Analytical method						
	Microscopy		Near-visible light		Spectroscopy		
Modification type	**Optical**	**Scanning electron**	**Ultraviolet**	**Infrared**[a]	**EDXRF**	**Raman**	**Profilometry (digital microscopy)**
Inlaying	No fiber disruption	No fiber disruption	n/a	n/a	No chemical difference	n/a	No fiber disruption
Scraping	No fiber disruption	No fiber disruption	n/a	n/a	n/a	n/a	No fiber disruption
Powder blasting or laser obliteration	No fiber disruption	No fiber disruption	n/a	n/a	n/a	n/a	No fiber disruption
Chemical erasure	n/a	n/a	No visible difference	No visible difference	No chemical difference	No chemical difference	No fiber disruption
Retouching small areas	No visible difference, no feathering	No visible difference, no feathering	No visible difference	Note 1	Note 1	Note 1	No visible difference, no feathering
Retouching the entire diamond	No visible difference	No visible difference	n/a	n/a	No chemical difference	No chemical difference	No visible difference

[a] The fluorescence noted under infrared light was confirmed by EDXRF and Raman spectroscopy to be from chromium found near the second 7s of all three Hugo cover stamps. As discussed in the text, this is believed to have been a contaminant introduced in the printing process.

no evidence was found of the addition or bleaching away of additional layers of pigment in order to change a '3' into a '7', or any fiber disruption (e.g. through deliberate tamper by scraping, cutting or the addition of fibers) during depth composition examination of the second '7 diamond' regions on any of the stamps examined. Again, there is no evidence that extra layers of pigment have been added in order to convert a '3' to a '7'. Individual fibers from the paper can be traced, again showing no evidence of tamper."

5. Dr. Hans Hagemann, University of Geneva[12]
   "Further inspection of the paper fibers do not suggest any mechanical action (scraping) on the stamps, in agreement with the observations in the 'Hall' report."

PLATE 77 RESEARCH

There is no doubt the three stamps on the Victor Hugo cover show a plate number 77 that originated from plate 73. The corner letters match, and the flaw in the "S" box of stamp SK is common on both the stamp and the imprimatur proof.

The fact that there is no evidence of tampering can only mean that Perkins, Bacon & Co., the printers of this issue, altered the plate numbers on some impressions from plate 73 to a number 77.

This procedure was certainly irregular, so why do it? Perhaps it was one of the following reasons:

- a failed experiment at a temporary repair or marker number,
- a misunderstanding between the printers and plate makers,
- an unauthorized act at Perkins, Bacon & Co.,
- an effort to make a collectable stamp, or
- a mixture of these.

In fact, 66 impressions on plate 73 are documented in both the Perkins, Bacon & Co. printing records and the Inland Revenue records as having been reentered.

As far as the origin of stamps showing a plate number 77, my research has revealed that there are only two possibilities for how these stamps came into existence (Najjar, 2008a, 2008b, 2009a, 2009b, 2009c).

According to the Inland Revenue document IR79/79, pages 41 and 42, held at the National Archives, plate 77 was not registered or put to press, and no sheets were printed from it when the issue went to press in March 1864. The plate was rejected in a letter from Ormond Hill, secretary at the Board of the Inland Revenue, to the printers Perkins, Bacon & Co. dated 7 February 1863 and was defaced in February of that year.

The first possible origin is from the rejected imperforate and ungummed trial sheet(s) printed over a year before this issue was put to press. The sheet(s) that should have been destroyed would have had to be stored, then perforated, gummed, and released amongst the ~13.2 billion stamps printed but not before someone knowing their importance removed the four known unused examples from the top of the sheet. This gives us odds of finding a used example, say, stamp PH from the one trial sheet released to the public, as high as 1 in 13.2 billion.

If these stamps did originate from the trial sheet(s), then one would expect the impression to be pristine and the plate numbers on all stamps to look identical in shape and position. They would also exactly match the roller impression from which they originated. However, close examination of all the accepted stamps showing a plate number "77" reveals that they do not (Figures 19 and 20).

FIGURE 19. Great Britain 1858–1879 1d red plate 77, an uninked impression taken from the transfer roller, the Board of Inland Revenue Stamping Department Archive, list 4, volume 12; plate 77, BA, unused, the Tapling Collection, Great Britain section, page 2 and plate 77, PH, used, the Fletcher Collection, volume 81, page 2. The black arrows indicate the two dashes next to each figure "7" on the roller impression. These are a fundamental feature of the master die yet are absent on both stamps BA and PH. Courtesy of the British Library Philatelic Collections.

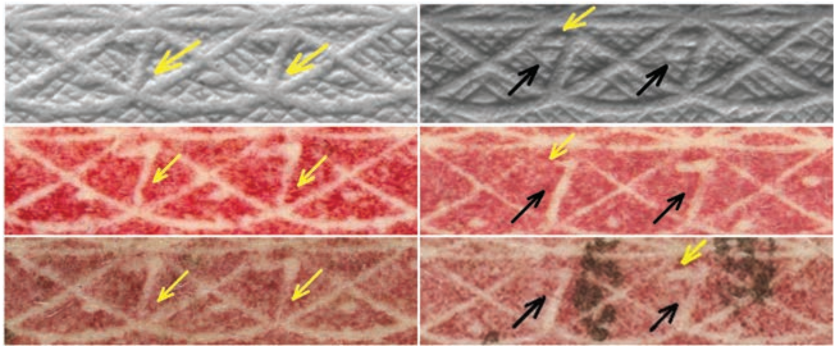


FIGURE 20. Left- and right-hand-side plate number "77" from the plate 77 roller impression plate 77 stamps BA and PH, respectively.

In fact, I have examined thousands of these stamps from every known plate, and the shape and position of the plate number do not vary in any way apart from the expected inking vagaries on some. This, however, is *not* the case with the accepted plate 77 stamps.

The right-hand column of Figure 20 shows the two dashes against each number "7" present on the roller impression, which are absent on both stamps BA and PH (black arrows), and the short and misshapen figure "7"s (yellow arrows). The left-hand column shows the dissimilar figure "7"s and, most important, the position on the intersection on which they fall (yellow arrows). These could not have originated from a trial sheet produced from this roller impression.

The second possible origin is through reengraving some existing plates with the number "77." Although this was quite an incredible procedure adopted by Perkins, Bacon & Co., this is a valid possibility because the existing plate 77 stamps show anomalies that cannot be explained by the trial sheet theory but can be explained only by reengraving.

The anomalies in the figure "77" on all the accepted plate 77 stamps cover are as follows:

- None of the figure "77"s match each other in shape and position as they should if they had originated from one roller impression.
- They lack a fundamental feature that appears on the master die.
- They show signs of wear that cannot be so had they originated from pristine trial sheets.

There are 13.2 billion stamps matching their plate numbers in shape and position, yet the few accepted stamps originating from the alleged proof sheet are all different. Why?

The alteration of the plate number to a number "77" could have been done by hand engraving directly on the plate, which would have been carried out either by the movement of the metal within the diamond area in order to produce the figure "7" or by the insertion of a plug on which the new number was engraved. Both methods have been replicated in the laboratory, proving that such an action could have easily been done by the master engravers of that time.

My research into the 1858–1879 issue and the origin of plate 77 stamps, the imprimaturs and the roller impressions, plate 73 and both the documented and undocumented plate repairs, the scientific evidence, and other matters relating to the Victor Hugo cover are fully published on my Web site.[13]

There is no doubt that the discovery of the Victor Hugo cover has caused a major controversy amongst philatelists and philatelic experts, a few of whom opted for the faking option in view of the incredible rarity of this major philatelic item and the way that these "plate 77" stamps were produced.

However, had it not been for my unwavering belief that the stamps and cover were completely genuine, the extensive use of state-of-the-art forensic science and scientific equipment and the involvement of internationally recognized forensic scientists, all of whom and without exception have found the stamps to be completely untampered with, then an extraordinary world-class philatelic gem of the greatest importance and the unique and most revealing research that it has generated would have been sadly buried for all time.

NOTES

1. Adrien Legedre, email message to author, 21 May 2012.
2. The British Library, 96 Euston Road, London, NW1 2DB, UK. http://www.bl.uk/, accessed 28 January 2013.
3. The British Postal Museum and Archive Freeling House, Phoenix Place, London, WC1X 0DL, UK. http://www.postalheritage.org.uk/, accessed 28 January 2013.
4. The Royal Philatelic Society London, 41 Devonshire Place, London, W1G 6JY, UK. http://www.rpsl.org.uk, accessed 28 January 2013.
5. The Philatelic Foundation is located at 341 West 38th Street, 5th Floor, New York, New York, 10018, USA. http://www.philatelicfoundation.org/ (accessed 28 January 2013).
6. The Forensic Institute—Glasgow, Baltic Chambers 50 Wellington Street, Glasgow, Lanarkshire, G2 6HJ, UK. http://www.theforensicinstitute.com, accessed 28 January 2013.
7. Reading Scientific Services Ltd., Reading Science Centre, Whiteknights Campus, Pepper Lane, Reading, RG6 6LA, UK. http://www.rssl.com/, accessed 28 January 2013.

8. Gene S. Hall, Ph.D., Professor of Analytical Chemistry, Rutgers–State University of New Jersey, Department of Chemistry and Chemical Biology, Wright-Rieman Laboratories, letter dated 1 April 2010.

9. Robert W. Radley, forensic handwriting and document examiner, M.Sc., C.Chem., F.R.S.C., F.S.Soc.Dip., F.A.E., R.F.P., the Forensic Document Laboratory, Macartneys, Kings Road, Silchester, Reading, RG7 2NS, UK, report on Plate "77" Stamps, dated 22 July 2009.

10. Report of Professor Allan Jamieson, B.Sc. Ph.D., CBiol FSB, Director of the Forensic Institute, Glasgow, UK, Consideration of the Evidence Relating to Stamps, dated 19 July 2012.

11. Mr. Tom Ray, Technical Specialist, Microscopy Laboratory manager, RSSL, letter dated 30 March 2010 and Examination and Analysis of Three Penny Reds—Penny Red 77, report dated 29 February 2012.

12. Dr. Hans Hagemann, Department of Physical Chemistry, University of Geneva, 30 Quai Ernest Ansermet, CH-1211 Geneva 4, Switzerland, letter dated 5 October 2010.

13. The Victor Hugo Cover–Plate 77 Web site. http://1dplate77.com, accessed 10 February 2013.

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The U.S. 1851 3¢ Stamp: Color, Chemistry, and Changes

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ABSTRACT. This paper describes research performed on the United States 3¢ 1851 stamp (Scott USA numbers 10, 10A, 11, and 11A) both to determine analytically the elemental composition of their printing inks and to demonstrate quantitative measures of their color with state-of-the-art technology. The principal analytical tools for performing these analyses were X-ray fluorescence spectroscopy (XRF) and optical reflectance spectroscopy. A relatively simple technique for determining significant elements in the ink pigment is presented based on XRF analysis. The resulting elemental data are then correlated with documented chemical formulae and visual properties of pigments and inks of the period. This correlation allows the likely and predominant pigments used in the manufacture of the inks to be inferred. From this, a general approach for the evaluation of ink colors in terms of likely pigments is offered. The use of rigorous scientific analyses led to results that challenge long-held historical beliefs about particular inks used for these stamps. The results were surprising and not predictable. The older hypotheses, while posited using a technical approach, did not have access to the types of analytical tools available today.

HISTORICAL BACKGROUND

The United States 1851 3¢ stamp is an important and popular philatelic collectible. It has been the subject of significant research for a long period of time. The stamps are distinguished for collecting purposes by the characteristic positions of the specific plate from which they were produced. Furthermore, over 1 billion stamps were produced during a 10-year period from 28 original or modified plates. This resulted in many plate varieties and color shades (Granzow, 2004:268). The specific colors of the stamps, a subject of much specialization, can often be associated with the plate used, the year of production, or both. The year of production is deduced from dates found on postal usages and through the years agreed upon by specialists studying these stamps. However, almost no scientific work has been done in the area of inks, pigments, and the resulting colors. Nonetheless, speculation and hypotheses have abounded and have become part of the documented philatelic history of the stamp.

What follows is the history of what was believed concerning the colors and their origins for the subject stamp prior to the work recorded in this paper being done. This work was done to explore the elemental content of the stamps of the period with no preconceptions influencing the selection of the tools or the plan of the experiments or the possible outcomes. Nor was there any preconception about what would be discovered.

In Chase's (1942:154–158) landmark book on the 3¢ stamp of the 1851–1857 period, he described in some detail the various colors of the stamps by year. The sequence

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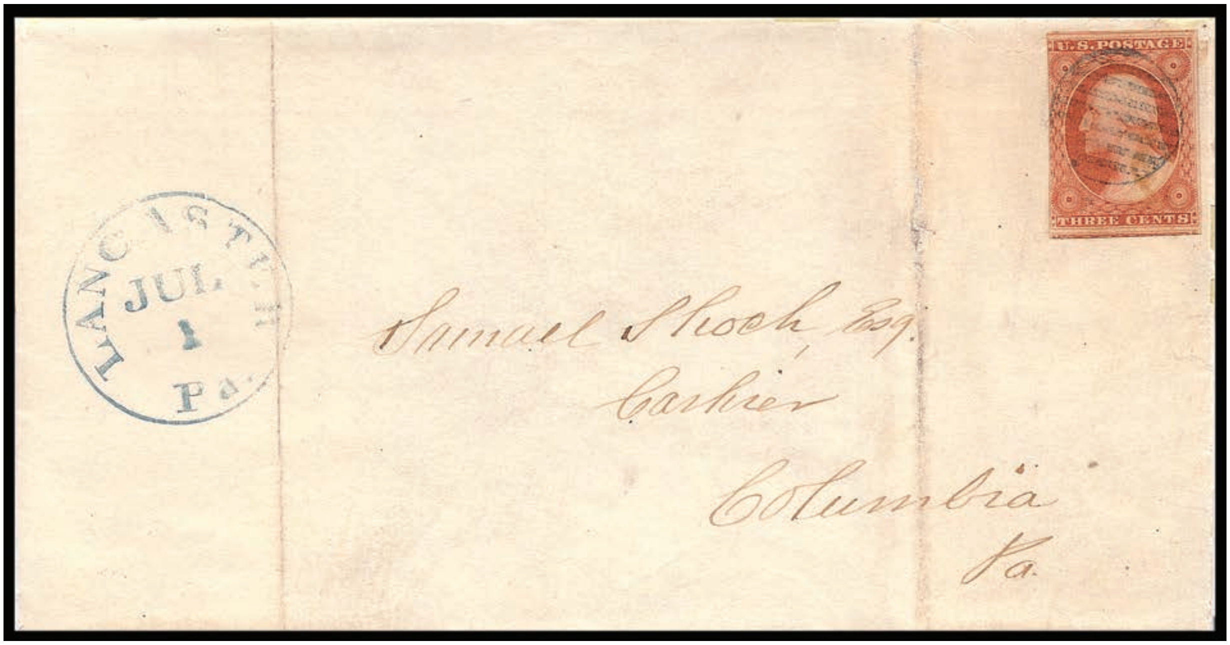

FIGURE 1. Orange-brown color (Scott 10A) first-day cover, 1 July 1851. Courtesy of the author.

discussed by Chase, the one we will follow covering the first two years or so, begins with the orange-brown stamps, then the brownish-carmine stamps, followed by the dull red stamps. Chase then proceeds to hypothesize how these colors were compounded or created. Chase eliminated most dyes and lakes based on observed stamp colors, commonly known printing practices, and pigment availability at the time of the 1851 stamp production. This was a very logical and thoughtful assessment of the options for color generation of the time. The authors followed a similar approach in their analysis but with much more access to historical information.

Chase then described experiments used to determine the primary pigment as Venetian red (an iron oxide–derived pigment, Fe_2O_3) augmented with vermilion (mercuric sulfide, HgS) to obtain a very rich, more orange color. Figure 1 illustrates an example of the orange-brown stamp used on a first-day cover dated 1 July 1851.

He also commented the pigments used were, for the most part, resistant to sunlight. He speculated the stamp pigment was approximately 80% Venetian red and 20% vermilion based on experiments using color matching with selected contemporaneous pigments. He further commented on the pigment sensitivity to atmospheric sulfur dioxide. Occasionally, this pollutant caused darkening of the stamps, which he noted could be remedied by treatment with hydrogen peroxide, H_2O_2. Chase continued, saying the next "serious" color was brownish carmine. This is the most common color produced in 1852, although it first appeared in the late fall 1851. Chase went on to say it was probably a very good quality Venetian red without admixture of the vermilion as was done in the early orange-brown pigmented stamps (Chase, 1942:156). Indeed, today this color would approximate the artist color known as Venetian red. Figure 2 shows the earliest documented example (22 October 1851) of the brownish-carmine color.

Chase continued, observing that soon after January 1853, another major color change occurred. The ink, he stated, "was somewhat suggestive of the original orange brown color, though the color is duller and impressions are never very clear" (Chase, 1942:156). Figure 3 shows an example of the dull red–colored stamp from the author's collection that was tested during the current research. Chase stated the pigment was Venetian red, though perhaps with less vermilion (Chase, 1942:156). This is his last mention of ink pigments for the stamps.

Those pigments, Venetian red, or similar iron oxide–based pigments, with or without vermilion (mercuric sulfide, HgS), were deemed the component bases of the remainder of the colors of the series. Nothing was later added about ink composition versus perceived color versus years of use, except for a relatively standardized naming nomenclature per color per year range.

POST-1942 COLOR EXPLORATIONS UNTIL NOW

Since the time of Chase's book publication in 1942, almost no technical work, much less scientific work, has been performed on the 3¢ 1851–1861 stamps. The only notable exception has been very critical visual comparisons, categorizations, and

FIGURE 2. Earliest known use, 22 October 1851, for brownish-carmine color (Scott 11A) (Plate 1 late). Courtesy of the author.

FIGURE 3. Dull red color (Scott 11A) identified by Chase (1942). Courtesy of the author.

naming of the 3¢ colors (Amonette, 1973; Beals, 1974; Amonette and Hulme, 2005). These works have become the basis of color standardization and naming in this area of specialization. The subject stamp was produced and used from July 1851 to the fall of 1861. As mentioned earlier, the 3¢ stamps were produced in many distinctive or slightly different colors, hues, and shades. However, it should be noted the term used to describe the color of this stamp by the Post Office Department was simply "red." This fact is documented in correspondence from the Post Office Department to the stamp contractor, Toppan, Carpenter & Co. (Toppan, Carpenter & Co., 1851).

COLOR DIFFERENTIATION AND NAMING

Color identification and matching have been done for the 1851 3¢ stamps for over 70 years. Starting with Chase's (1942) work, specialists have continued to study the colors. This has included Card (1964), Amonette (1973), Beals (1974), Amonette and Hulme (2005:103–109), and James Allen.

Significant collections of these stamps, starting with those of Chase, have been retained and extended by today's specialists. Through the years, additional stamps would be sent to all of the experts on this issue for identification. The colors were then agreed to by these experts, thus becoming a de facto standard. Standard color charts were then prepared using actual stamps. These charts can be used to perform color matching on unknown samples.

INK FORMULATION IN THE MID-NINETEENTH CENTURY

During the period 1851–1861, based on actual practice, oil-based inks for banknotes, paper, and stamp production were fairly similar in composition and manufacture.[1] The banknote inks were usually black and carbon based. Beyond the mid-nineteenth century, 1856 in the case of Toppan, Carpenter &

Co., color began to be used more. The inks were composed of a liquid vehicle that was combined with the dry pigment portion of the ink.[2] The liquid portion consisted primarily of linseed oil, often a blend of viscosities. It might also include a higher heat treated, slightly oxidized oil component called a varnish to modify viscosity and aid in adhesion. Finally, other ingredients were often included: a drying agent, a very volatile hydrocarbon to facilitate mixing and wetting of the pigments, a wax to modify flow properties, and a few other proprietary ingredients. The actual solvent recipes are rarely found or are nonexistent. Pigment recipes for early stamps are rare and proprietary. That was all part of the craft at the time. Vehicle properties were tailored to the needs of the final ink properties desired and the specific incorporated solids. Attention was paid to the ability to mix the ground pigments thoroughly into the vehicle. These were, by nature, complex mixtures that required recipes and significant knowledge and skill of the ink maker. Inks for the banknotes were compounded "in house" most of the time and were modified as needed during production. Carbon-based black inks could be purchased premixed depending on the nature of the ink and printing desired. Colored inks, however, often required mixing on site for technical reasons. The ink recipe formulations, including the pigments used, were often proprietary in nature.

Opaque, semiopaque, and translucent inks were engineered to give rise to dried films of particular characteristics such as opacity, carefully designed hues and shades, reflectivity, adhesion, drying characteristics, and long-term stability, all the while with attention paid to cost. Many pigments or inks in this period were relatively expensive. Solid ingredients such as extenders were used essentially to produce more of the ink through basic dilution while not sacrificing the body of the ink or altering the color any more than necessary. Other solids might be added to change the tint of the final product or were added to maintain the effect of translucency because of selected refractive or reflective properties. Still other pigments were added to increase opacity. All pigments had some of these characteristics to effect change and had to be carefully selected and formulated to get the desired effects. A good summary of many of the elements and pitfalls of ink production, albeit derived from a later banknote period but that are nevertheless applicable to the 1851 decade, has been written by Sayers (2009).

Most of the pigments of this period were either ground naturally occurring minerals or chemically prepared, precipitated compounds. Ground, mined pigments were already declining in relative usage volumes compared to the growing uses of chemically synthesized versions. Chemically prepared pigments appeared by the 1820s, and by the late 1860s significantly more were introduced. This was facilitated by the growth of the German chemical industry for producing chemical dyestuffs. For all practical purposes, only a few natural dyestuffs were available during the time period considered and were not used in the formulation of the ink for these stamps. This will be discussed later in the pigment determination section.

EXPERIMENTAL SETUP

The experimental setup includes both the selection of stamps for analysis and the selection of analytical hardware. These are described in the following sections.

Sample Selection

This research was limited to 3¢ 1851 stamps issued during the first 24 months of usage. The specific stamps selected for testing represent the five important colors of this early period. Those colors are orange brown, the experimental orange-brown color with the mid-1852 color being a variant, brownish carmine, the 1852 claret, and dull red. They were selected based on standards discussed in the "Color Differentiation and Naming" section above. The reader should consult the references for more information. Colorimetric and XRF analyses were then performed on each test sample as described in the following section. The elemental compositions of the ink were then used to deduce the pigments that were used in the ink formulation. This inference was drawn by considering historically used pigments, their commercial availability, and their color characteristics. For this paper, 11 stamps were selected to illustrate the experimental procedures and results interpretation. For identification, these were labeled Sample A to Sample L (no Sample I). Results of the analyses of these samples are given in subsequent sections.

Hardware Selected for Performing the Analyses

As introduced above, two analytical devices were selected for this research. The first was the Video Spectral Comparator (VSC 6000),[3] (Foster + Freeman, Ltd., 2011), and the second was the Bruker Handheld Tracer III-SD X-Ray Fluorescence Analyzer.[4] Both of these devices, located at the Smithsonian National Postal Museum in Washington, D.C., are described very briefly below.

The Video Spectral Comparator (VSC 6000)

The VSC 6000 is an analytical device that can perform many different forensic analyses on paper documents. It has a number of functions that are ideally suited for the analysis of philatelic material. The capability used for this research was to determine the reflectivity of sample stamps under light with wavelengths from 400 to 1,000 nm. This range includes visible light and near-infrared and near-ultraviolet wavelengths. More important, the VSC 6000 can provide quantitative measures of colors, or colorimetry analysis, based on the CIE color standards.[5]

Bruker Handheld Tracer III-SD X-Ray Fluorescence Analyzer

For elemental analysis of the ink on the subject stamps, a Tracer III-SD X-ray fluorescence analyzer was used. This spectroscopic device uses X-rays to excite electrons in the atoms in

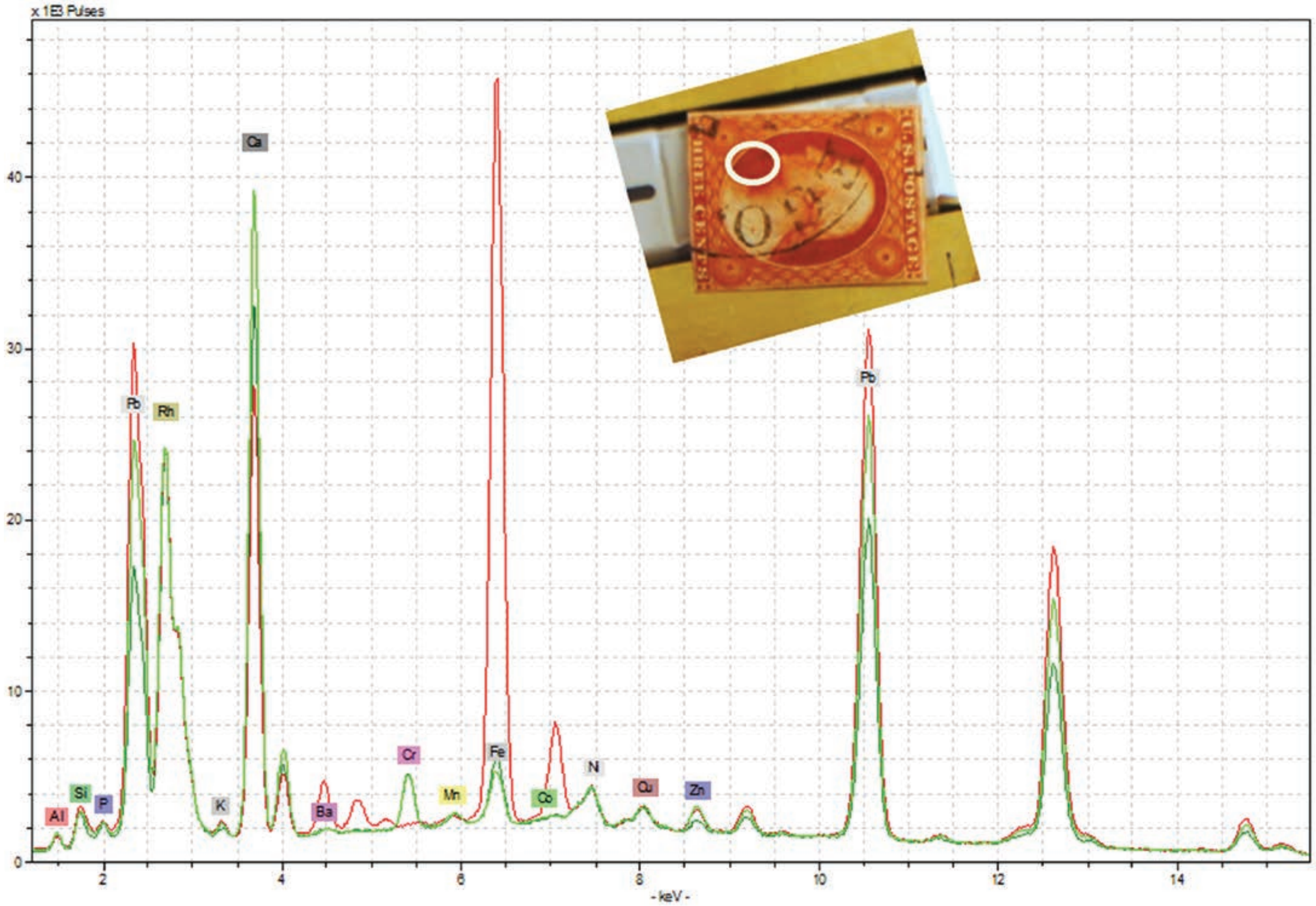

FIGURE 4. Typical X-ray fluorescence spectrograph, illustrating portion of stamp ink for three different samples of Scott 10A. The white oval on the inset stamp is the approximate sample size. Courtesy of the author.

a specimen to be analyzed. These atoms then emit photons that can be counted. Each chemical element emits photons at different energy levels. The number of counts for each energy level, measured over a given sampling period, indicates the amount of various elements present in a sample. Figure 4 illustrates a typical spectrograph that results from the XRF analysis. Software that is part of the testing device produces the spectrographs and also helps identify the specific elements present.

It is also possible to describe elemental content by the number of counts for each element. This method will be used subsequently in this paper.

EXPERIMENTAL RESULTS

As noted above, two types of analysis were performed on each of the sample stamps. The first was an analysis of color using the VSC 6000, and the second was an analysis of chemical elements using the Bruker XRF. The results are presented in this section.

Color Analysis

The VSC 6000 was used to measure the reflectivity of all of the sample stamps. Figure 5 illustrates the range of stamp colors that were obtained by this testing. While five major colors were highlighted for testing for elemental analysis, a much larger sample was used merely to explore the range of color variations as detected by the VSC 6000 colorimeter. The 33 points correspond to measurements at three different locations on each of 11 different stamps selected for color variations, which included heavily inked areas and lightly inked areas that would include more color influence caused by the paper. Figure 5 also shows a small ellipse. This is called a MacAdam ellipse. It represents an estimate of a discernible range of colors that an individual perceives as being the same

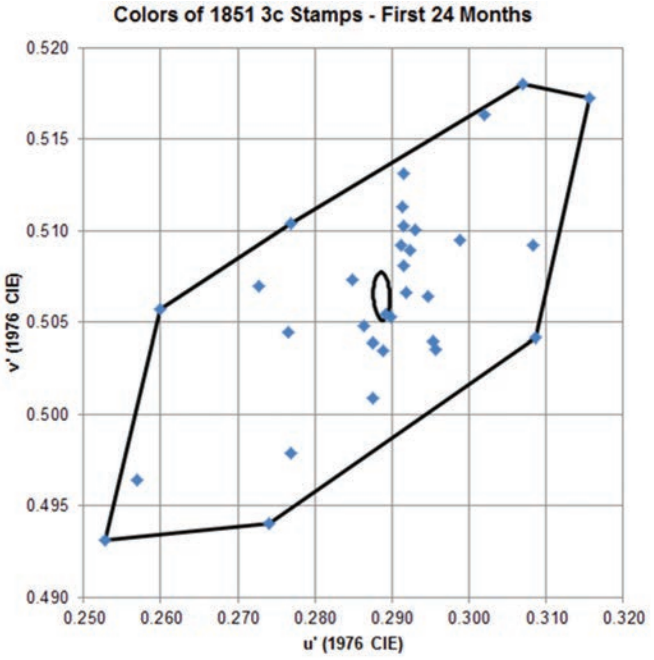

FIGURE 5. Chromaticity plot of 1851 3¢ stamps.

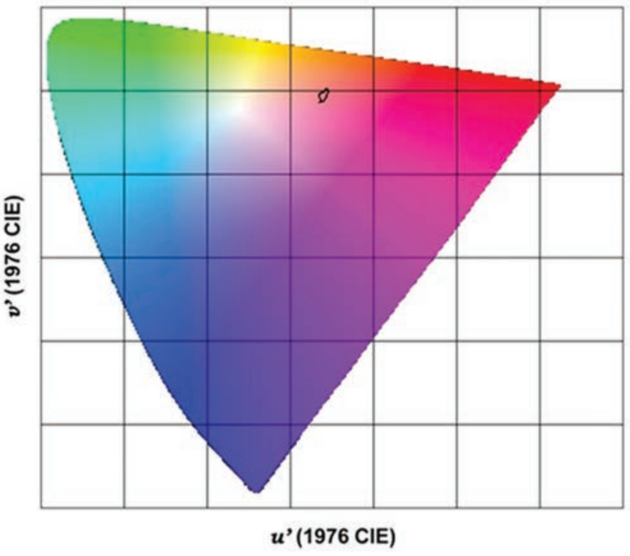

FIGURE 6. Location of 3¢ stamp colors in full 1976 CIE color gamut.

(MacAdam, 1942; Wyszecki and Stiles, 2000:308; Herendeen et al., 2011:108). The size of the color gamut of the measured stamps is many times the size of the MacAdam ellipse.

Thus, there are definitely many different, and discernible, colors of the stamps examined. Figure 6 shows the location of the measured colors on the CIE uniform chromaticity scale (Billmeyer and Saltzman, 1981, chapter 2). Visual analysis of the stamps and their resulting positions logically followed the "warmth or coolness" expected from the color gamut in Figure 6. Future work with this technology will explore the value of these analyses for evaluating standard colors. Overall, these stamps were classified as "red" when specified by the Post Office Department back in 1851, and certainly they fall into that part of the spectrum as shown in Figure 6, with a bias towards "brown or orange" as they are observed today.

In simple terms, the plot in Figure 6 also shows, in the "plus square" near the top, the location of the colors of the 3¢ 1851 stamps tested under the current research on a full gamut of perceivable colors. As noted, this research restricted the detailed analysis and discussion to the first 24 months or so of issuance, specifically addressing the colors mentioned previously that were identified by Chase and the other students of the 1851 issue.

XRF Analysis

When using XRF, the X-rays generally penetrate the whole stamp. As a result, the elemental composition of the paper is also being measured. This research performed testing to correct for any errors that this might introduce. All samples were irradiated for 180 seconds, and the resulting photon counts were recorded. Basically, the stamp is irradiated with measurements taken front and back on inked and very lightly inked or uninked portions of the stamp. By comparing the photon readings between the front and back, with a check when possible on the marginal paper that is not inked, one can ascertain the base number of photon emissions coming from elements in the paper. To correct for these effects, one can subtract the resultant photon measurements of the back from the photon measurements from the front. A titanium filter (called a blue filter) was used to measure the reflected photons from Mg, Al, Si, P, Cl, S, K, Ca, V, Cr, and Fe and any L and M lines for the elements that fall between 1.2 and 6.5 keV. All photons beyond 6.5 keV were filtered out.

Accounting for Paper Chemistry

During stamp production, sheets were routinely stacked in piles to complete the drying and curing process or for storage prior to gum application. As a result, the backs of the stamps may have pigment traces. While these are actually contaminants, and perhaps not visible, they could still be sufficient to be detected by XRF. Such photon readings can be mistaken for paper elemental content. However, the counts here are fairly low relative to those measured on the front of the stamp. Thus, they have no significant impact on the conclusions.

The Pigments

Likely pigments and their properties were determined by studying various key reference texts (Eastaugh et al., 2008; Higgitt et al., 2005) and then selecting possible pigments based on elemental content. Those candidates were then researched further based on their relevant color and probability of use during the 1851–1861 period.[2] Pigment properties were also assessed as to their chemical and light stability. Thus, obvious fugitive colors that are very sensitive to environmental factors were eliminated. The likely pigments are mineral based and all were also available chemically produced at the time. While a few of the available pigments arose from mining, these were generally of lesser quality. In either case, XRF identifies the important elements in the pigment and results in the same basic conclusions. Another important observation is the analyst can glean additional valuable information about possible pigments by noting which elements are *not* present in the XRF scans.

The commercially available dyes in the general color family of this particular period used to any significant degree were natural products. These included, for example, brazilwood, logwood, cochineal, and madder. Pigments derived from these products had a number of problems, including the following:

- They could be fugitive;
- They could become unstable in the presence of other pigments;
- They could bleed into the other pigments or the paper; and
- They were the wrong color match for the finished stamps, at least when viewed in the current era 155 years after the stamps were printed.

Additionally, the “laking” processes at the time utilized primary flocculation of the colors on amorphous aluminum-based substrates with calcium salts (Ellis, 1940:158–159). Aluminum is one of the most widespread elements in the universe and is expected to appear in all elemental analyses of mixed products. Therefore, the presence of more than a trace of aluminum would be a requirement for most of the red lakes. This result was not found for the samples tested. Calcium salts, which are present in nearly all lake pigments, were present in all the pigment portions of the stamps tested. However, calcium could be expected to be present in the paper as well as a consequence of the preparation water (but only at very low levels). Water sources for paper production during this period were selected for overall low mineral content. Calcium salts are likely candidates as a filler or colorant in any paper, usually in the form of calcium carbonate ($CaCO_3$).

The Orange-Brown Shades

Figure 7 shows a range of orange-brown stamps used in the early period of the 1851 3¢ issuance. Dated orange-brown-colored stamps range from 1 July 1851 to mid-1852 or a little later, but few orange-brown stamps are found after March 1852. They originated primarily from five plates. Table 1 presents the XRF results, giving photon counts for various elements. We observed that all the orange-brown stamps of the 1851 period that were sampled contain primarily iron as the principal elemental colorant source. Iron oxide (Fe_2O_3) is the clear choice from the historical pigment considerations. This pigment has what is called a high extinction coefficient. This means it imparts color very effectively at low volume or weight because it is intense and saturated as determined by eye or machine. The artist color and name and ink color today would be similar to that named burnt sienna.

At the time of the 1851 stamp, Venetian red was the most common reddish brown earth pigment. It varied in shade and hue depending upon the manufacturer and whether it was mined from the earth as hematite or chemically produced. Today Venetian red as a named pigment is much redder and darker. It is an earth pigment, and while it was still mined in the 1850s, it was becoming widely available as a synthetic, having been manufactured chemically for over 50 years at the time the 3¢ 1851 was produced. Chemically manufactured pigments were preferred by the 1850s and earlier because of their typical higher quality, consistency, and minimum contaminates. By 1850, all calcium and lead salts that might be used in pigments or extenders were chemically prepared and relatively pure. The red lead chemical

Sample A Sample B Sample C Sample D

FIGURE 7. Representative orange-brown stamps used for testing. Courtesy of the author.

TABLE 1. Chemical elements in orange-brown stamps, photon counts at 180 seconds, all corrected for paper content.

Stamp	Calcium (Ca)	Iron (Fe)	Lead (Pb)[a]	Sulfur (S) (blue filter)	Other elements
Sample A, position 59L1 early; yellowish orange brown; earliest color, 1851	54,000	96,000	99,000	4,400	0 Mercury (Hg)[a]
Sample B, position 7R1 early; orange brown; first two weeks of production, 1851	170,000	360,000	332,000	6,500	0 Mercury (Hg)[a]
Sample C, position 92R1i; orange brown; 28 Nov 1851	50,000	101,000	80,000	4,500	0 Mercury (Hg)[a]
Sample D, position 91R2 early; orange brown; early 1852	88,000	310,000	152,000	6,500	0 Mercury (Hg)[a] 8,000 Barium (Ba)[a]

[a] Results from the L1 energy level.

process, for example, had been around for hundreds of years. The calcium salts used were all white and uniform. Any iron oxide variations due to sourcing, whether mined or chemically prepared, would then require more fillers and extenders in an attempt to achieve consistent shades and hues.

Table 1 shows that one of the inks contained barium (Ba). The sample shown was not a single occurrence. Barium sulfate ($BaSO_4$) is slightly opaque and white in color and was commonly used as an extender to dilute the more expensive pigment in the ink. It was commonly synthetic but could be mined as the mineral barite. No barium pigment at the time was colored other than white except for barium chromate ($BaCrO_4$), and the samples tested did not show chromium. Given the small amount of sulfur present, this should be attributed to the barium sulfate component, which is likewise small, and the calcium salt would likely be predominantly calcium carbonate. Calcium carbonate ($CaCO_3$) and calcium sulfate ($CaSO_4$) were and are both used to extend inks and to tint them because they are white in color. However, they have low refractive indexes and are not very efficient in tinting or achieving opacity, thus leaving an ink more translucent. Simple calcium salts such as the ones mentioned are all white but less so when dispersed in linseed oil. Varieties and ranges of particle size and oil take-up of the extenders were used to affect handling characteristics and final refractive indices of the ink.

The Experimental Orange Brown

Figure 8 shows samples of the experimental orange-brown color used for testing. Table 2 shows the elemental content of these samples. This color was suddenly introduced in early October 1851, for reasons still unknown. It is suspected to be related to the issues surrounding the original orange-brown pigment and is the subject of ongoing research.

Sometime after Chase's (1942) publication, many students began to realize in fact this was a significant color variety that was in effect for about five months, even if it was a relatively


Sample E
Sample F
Sample G
Sample H

FIGURE 8. Representative experimental orange-brown stamps used for testing. Courtesy of the author.

TABLE 2. Chemical elements in experimental orange-brown stamps, photon counts at 180 seconds, all corrected for paper content.

Stamp	Calcium (Ca)	Iron (Fe)	Lead (Pb)[a]	Sulfur (S) (blue filter)	Other elements
Sample E, experimental orange brown; 8 Oct 1851, second earliest date	260,000	0	650,000	12,000	0 Mercury (Hg)[a]
Sample F, 1852 brownish carmine, position 4R3; 28 April 1852	114,000	0	462,000	9,200	0 Mercury (Hg)[a] 5,000 Barium (Ba)[a]
Sample G, 1852 claret; 2 Feb 1852	110,000	0	420,000	12,000	0 Mercury (Hg)[a] 5,000 Barium (Ba)[a]
Sample H, early, dull red (unused)	90,000	4,000[b]	150,000	8,500	0 Mercury (Hg)[a]

[a] Results from the L1 energy level.

[b] Contamination suspected from orange-brown pigment.

scarce color change in the broad scheme of color groups based on populations. As a result of this research, it has been determined that the experimental orange brown was not just a variation of orange brown but was in fact foreshadowing a major change in color schemes and pigment chemistry.

It is noted some of these experimental orange-brown stamps contain barium (Ba). One sample contained iron (Fe), which could be a cross-contamination from the orange-brown ink that was still in production at the time. That sample, Sample H, is what is classed as a mid-1852 orange brown, which is duller in shade and does not fit into other color classifications. The iron-based pigment continued to be used on select plates, or at least stamps appearing on dated letters, well into 1852, dropping quickly in numbers into the year, being replaced by several lead-based pigments and colors.

Later Shades

Table 3 shows the XRF results for three stamps printed after the experimental orange brown introduction, as shown in Figure 9. The results show that the move to lead-based pigments continued. The brownish carmine of 1852, which is considered the primary color for the year based on populations (Amonette, 1973; Amonette and Hulme, 2005), and the 1852 claret, a lesser color variety introduced in late 1851 and discontinued in early 1852, both utilized primary lead-based systems with no significant iron (Fe) present in the inks. The iron (Fe) present in the brownish-carmine sample is likely from the blue cancel common to the period, iron ferrocyanide (Prussian blue). Sulfur is also present and likely attributable to the filler calcium sulfate, $CaSO_4$. Noteworthy is the fact that Sample L, the characteristic "dull red" color of late 1852 extending well through 1853 and beyond, contains not only sulfur (S) but also chromium (Cr). This was the first sample detected to contain chromium in these early years. The likely source is lead chromate ($PbCrO_4$), which is normally yellow, but orange and red varieties also exist. Again, red lead is a possible candidate for the primary "red" color, augmented by whites and possible yellow or orange. It is highly unlikely that the initial color mixed was quite this dull based on the known color chemistries. It should be noted that no mercury (Hg) is

TABLE 3. Chemical elements in later shades of stamps, photon counts at 180 seconds, all corrected for paper content.

Stamp	Calcium (Ca)	Iron (Fe)	Lead (Pb)[a]	Sulfur (S) (blue filter)	Other elements
Sample J, 1852 brownish carmine, position 4R3; 28 April 1852	138,000	<10,000[b]	353,000	6,600	0 mercury (Hg)[a]
Sample K, 1852 claret; 2 Feb 1852	127,000	0	397,000	7,700	0 mercury (Hg)[a]
Sample L, early, dull red (unused)	190,000	0	300,000	10,000	0 mercury (Hg)[a] 15,000 chromium (Cr)[c]

[a] Results from the L1 energy level.

[b] Contamination suspected from orange-brown pigment.

[c] Earliest historical evidence of appearance of chromium in these pigments.

FIGURE 9. Representative stamps of shades in postexperimental (later shades) orange-brown period used for testing. Courtesy of the author.

present in any of the samples in the data tables. Sampling stamps across the entire 10 years has revealed no mercuric sulfide presence. The lack of the presence of mercury indicated the lack of the presence of the pigment vermilion (HgS), which had been hypothesized 80 years earlier and is repeated often in the philatelic literature. However, the practitioner should also note that vermilion can be present in cancellation inks and must be taken into account with any element measurements.

CONCLUSIONS

There are three groups of conclusions for this study: the use of the analytical equipment, the results of the pigment and color analyses, and new discoveries made during the research. These are described in the following sections.

Analytical Equipment

There are three major conclusions relating to the experimental hardware used for this study. They are presented below.

- The Video Spectral Comparator (VSC 6000) has proven capable of determining quantitative color measurements for the 1851 color shades in line with human visualizations in a limited but meaningful way.
- X-ray fluorescence spectroscopy (XRF) has been shown to be a useful tool for elemental analysis, which helps to define pigment composition differences for the United States 1851 3¢ stamps.
- XRF is particularly effective in proving what elements and, by inference, which pigment is not present in a stamp ink.
- When performing experimental measurements, care must be exercised in determining, and correcting for, elements within the paper of the stamp as well as other inks on the stamp arising from cancellations or markings.

Pigments

- The primary pigment colorant for the initial 1851 orange-brown (Scott USA numbers 10 and 10A) (Scott Publishing Co., 2012) stamp appears to be iron based, probably iron oxide in natural or man-made form. It is listed as primary because of its dominance.
- The secondary pigment(s) used to augment the 1851 orange-brown pigment is lead based and is likely red lead (Pb_3O_4). It is a major component of the ink. It is listed as secondary because of less coloring capacity or remaining influence compared to the iron oxide.
- Several extenders and possible tinting agents seem to have been used in the first 24 months, notably $BaSO_4$ and $CaCO_3$, with minor impurities not assignable to significant pigments of the time.
- The brownish-carmine stamp pigments of the early period, fall 1851, were also a primarily lead based system, likely red lead. Clear evidence of dyes or dye lakes (such as significant aluminum content) is not readily apparent. Assuming the lake colors are visible at all, such colors were derived from dyes available at the time, and while they are inconsistent with the hues achieved in the finished stamps as they are viewed today, they cannot be eliminated from consideration.
- No iron, in any form, was found in the brownish-carmine stamp pigments of the early period.
- A base level of iron was always found in these earlier stamp papers.
- The dull red of the late 1852 and early 1853 period is also predominantly lead based with a variety of extenders and diluents, varying in proportions.

New Discoveries

- The experimental orange-brown color represents a major pigment transition heretofore not recognized other than by the appearance of an odd color. The pigments for the experimental orange-brown stamps are lead based and not iron oxide based like the original and associated orange-brown stamps, contrary to popular understanding. Iron content is basically nonexistent in the pigmentation of these stamps.
- Given the elemental analysis of the stamps and their dates of use, the move to the primarily lead based system and away from the iron oxide–based system used for the initial orange-brown stamps must have likely been made in mid-September 1851 or earlier.
- While cadmium pigments were coming onto the colorant scene during this period, no cadmium was found in the pigments, even at trace levels, over the 10-year span studied.
- Contrary to historical accounts and speculation, *no* vermilion or mercuric sulfide sources have been detected in the 1851 3¢ series of stamp color varieties in the first 24 months of issuance of the subject stamps tested. Vermilion is not the "orange" color modifier for the Venetian red (iron oxide) as has been stated and often repeated over the last 80 years in the literature.

NOTES

1. While the two cited references (Eastaugh et al., 2008; Higgitt et al., 2005) are most useful, there are no single reference sources that adequately cover the pigments, and their chemical and physical properties, for this period. More than 50 artist, museum, pigment, and historical books, articles, and Web sites were used. Those appearing to provide consistent information were considered reliable. The most difficult data to find was a description of which pigments were used during the period of study and when they may have been introduced. An especially useful Web site that provides much basic information is http://www.webexhibits.org/pigments/, titled Pigments Through the Ages (accessed 1 March 2013).

2. In the ink industry, the term "vehicle" is traditionally used for the liquid material holding and carrying the pigment and providing good workability on the press. Vehicles for intaglio inks may include oils, solvents, binders, and the like. Historically, linseed oil was the primary vehicle for mid-nineteenth century inks.

3. The Video Spectral Comparator 6000 is a spectrophotometric device used primarily for forensic document examination. It is manufactured by Foster + Freeman, Ltd. of the United Kingdom and United States. For more information, see http://www.fosterfreeman.com (accessed 1 October 2012).

4. The Bruker Tracer III-SD X-Ray Fluorescence Analyzer is a portable X-ray fluorescence spectrometer that allows unknown samples to be analyzed for their elemental composition. For more details, see http://www.bruker-axs.com/handheld-xrf-analyzers.html (accessed 1 October 2012).

5. CIE, the Commission Internationale de l'Éclairage (International Commission on Illumination), formed in 1913, is the international organization that develops standards for everything having to do with light and color. They have had a number of color standards through the decades used for color matching. For more information, visit their Web site at http://www.cie.co.at/main/ (accessed 1 October 2012).

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Analysis of Postage Stamps by Proton-Induced X-Ray Emission Spectrometry

Thomas E. Gill

ABSTRACT. Subtle variations in ink color and paper of postage stamps can affect their value and desirability to collectors and investors. Proton-induced X-ray emission spectrometry (PIXE) is a generally nondestructive forensic analysis tool that reveals the concentrations of chemical elements in a sample. PIXE has been used for more than 30 years, sometimes in conjunction with other analytical methods, to differentiate philatelic printing techniques; to quantify differences between different shades, varieties, and reprints of stamps; and to separate genuine stamps from forgeries. This paper reviews the history of philatelic paper and ink analysis by PIXE through a focus on case studies from the 1980s to the present. For example, PIXE has been used to show distinct chemical signatures between genuine stamps from China, Czechoslovakia, Eastern Silesia, South Africa, South-West Africa, and Taiwan and forgeries thereof. PIXE analysis showed how variations in ink chemistry control color shades of stamps from Mexico and reveal the origin (country of printing) of Iranian stamps, suggesting early (pre-twentieth century) utilization of organic inks on European-printed stamps from both nations. The technique was utilized to determine variations in paper types on stamps from China and Taiwan and how original People's Republic of China stamps from the early 1950s can be separated from modern reprints. The paper concludes with a PIXE investigation of Mexico's 1895–1898 "Mulitas" stamps. The analysis reveals that unlike previous Mexican issues, the Mulitas were printed with organic-based inks on largely clay-free papers. Differing amounts and/or formulations of metal (zinc, lead, and titanium) oxide whiteners apparently controlled the present-day color shade of the stamps, either directly or indirectly, with bluish inks having relatively more zinc and lead and greenish inks having relatively more titanium.

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 and the chemical and material properties of papers and inks. Potentially subtle variations in ink and/or paper of stamps with otherwise identical designs may affect their value and desirability to philatelists and investors or reveal them to be forgeries or reprints. Because of its ability to nondestructively reveal elemental compositions, proton-induced X-ray emission spectrometry (PIXE) has long been an applicable technique for analysis of a variety of historical inks and papers (Cahill et al., 1981; Johanson, 1989; Demortier, 1991; Hassanzadeh et al., 1999) and has been used for analysis of postage stamps from the technique's early days to the present (e.g., Cahill et al., 1981; Malmqvist, 1986; Almquist, 1985, 1986, 1988; Johanson et al., 1986; Hall and Lee, 1990; Johanson, 1992; Cheng et al., 1996, 1998; Pillay, 2000; Gill, 2007; Oliaiy et al., 2009; Voltr and Nejedly, 2012).

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PROTON-INDUCED X-RAY EMISSION SPECTROMETRY

Proton-induced X-ray emission spectrometry was developed in the 1970s as a multielemental analysis technique that is generally nondestructive; requires minimal or no sample pre-preparation; and is quantitative, fast, and sensitive (Pillay, 2000). It is conceptually similar to X-ray fluorescence spectrometry (XRF), which has also been used for analysis of stamps (Preiss and Robie, 1982; Cesareo and Brunetti, 2008; Jelovica Badovinac et al., 2010), but with PIXE a beam of protons, generally with energy of millions of electron volts (MeV), is used to bombard a sample. A particle accelerator, usually a Van de Graff accelerator, cyclotron, or similar machine, is used to create the proton beam; thus, PIXE facilities generally exist only at specialized academic or national nuclear laboratories (Johanson, 1992) and are less ubiquitous and much more costly than XRF. The high-energy proton beam ionizes some of the atoms in the sample. Some of the electrons in the inner shells orbiting the sample's atomic nuclei are knocked away, creating a "hole." In response, other electrons "drop down" from outer orbitals of the atom to "fill the hole" and take the place of the ejected electrons. In the process, X-rays with a constant and unique energy for each such transition (characteristic X-rays) will be emitted (Johanson, 1989). Each chemical element will typically have several unique, characteristic X-ray emission energies. This discovery, made by Moseley 100 years ago, led him to suggest that emitted X-ray spectra could be used for chemical analysis (Moseley, 1913). These X-rays are measured by a detector and converted to electronic signals, and software is used to calculate the concentrations of the individual elements within the analyzed part of the sample from the number of X-rays detected with each characteristic energy. The higher energy of the proton beam used in PIXE, as compared to the X-ray beam in XRF or electron beam from an electron microprobe, allows for higher sensitivity than these other techniques, detecting smaller concentrations of a material's constituent elements more quickly.

Although all detectable elements are quantified simultaneously, the PIXE technique allows detection only of elements sodium and heavier, so the lightest elements such as carbon and oxygen cannot be analyzed directly by PIXE. PIXE successfully detects a number of relatively light elements such as aluminum (used as a sizing agent for some philatelic papers) (Lera et al., this volume) and magnesium (also found in some philatelic papers) (Almquist, 1988) not determined by X-ray fluorescence. The technique works best for quantifying elements with atomic numbers between 20 and 30 (Johanson, 1992), including calcium and the "transition metals" such as iron and zinc (common components of printing inks and papers), where concentrations as low as a part per million or less can be routinely detected (Johanson, 1992). Samples that are thin and flat, such as postage stamps, provide ideal surfaces to be analyzed by PIXE. The actual detection limit (minimum concentration of an element detectable in the sample) will depend on the energy of the beam and the length of time the sample is exposed to the beam. Samples may be analyzed in a vacuum; in a chamber filled with helium, argon, or another gas; or in air (the "external beam" technique often used for philatelic applications [Almquist, 1985; Hall and Lee, 1990; Voltr and Nejedly, 2012]). The proton beam generally penetrates only an ultrathin layer on the surface of the sample. It will not pass through the paper of a postage stamp or envelope, thus revealing the composition of the printing ink or, when the beam is placed on a portion of the stamp clear of the design, the paper. The size of the beam determines which part of the sample is analyzed at any given moment. Most reported philatelic analyses have been of spots on the stamp several millimeters in diameter ("proton milliprobe"), although the beam can be focused down to pinpoint tiny areas on the order of a micrometer in size ("proton microprobe") or moved across the sample to provide its overall composition. X-ray spectrometric techniques can also often be useful to determine what elements are not present in an ink or paper (beyond a minimum concentration), in addition to what elements are present (Allen and Lera, this volume). This is especially true for PIXE, with its relatively low minimum detection limits for many elements.

A potential disadvantage of PIXE is that it is purely an elemental analysis technique. PIXE cannot reveal the crystal structure or molecular species in which an element resides, which has led to controversies in its application for analysis of historical documents such as the titanium contained in the Vinland map (Skelton et al., 1995).[1] With regard to the detection of fakes and forgeries, PIXE data can only show that the elemental concentrations and ratios are consistent with a known ink or paper, not always conclusively proving the (in)authenticity of a given item. PIXE relies on proton beams of high energy, typically in the millions of electron volts. This is an advantage in that it can detect lower concentrations of elements than other techniques such as X-ray fluorescence. However, it also represents a disadvantage in that prolonged exposure to the beam, longer than a few minutes, could burn or otherwise damage fragile materials such as paper (Cahill et al., 1986; Hall and Lee, 1990; Xeng et al., 1990; Demortier, 1991; **Sánchez**, 2006). Hall and Lee (1990) sandwiched the stamps they analyzed between thin layers of Kapton film and still observed some damage after five minutes of exposure to the proton beam. Voltr and Nejedly (2012) examined stamps by PIXE at reduced pressure in an argon atmosphere to decrease the potential radiation damage compared to analysis in a vacuum, while still allowing a quantitative analysis. When used carefully, however, PIXE is a nondestructive method of testing. The experiences of multiple investigations (as described throughout this paper) show that a thorough and ample PIXE analysis should be obtained within a few minutes of irradiation, which would not risk damage to the stamp.

Although PIXE has been used most widely in materials science, environmental studies, and biological and geological investigations, it was recognized early on as a powerful tool for historic and forensic analyses of inks and papers (Cahill et al., 1981; Thompson, 1983; Kusko, 1988), especially after it was used to reveal the printing methods and materials of the "Gutenberg Bible" (Schwab et al., 1983). Since then, reviews of this technique inevitably mention its application for analysis of historical printed documents (Johanson, 1989, 1992; Demortier, 1991; Pillay, 2000; Vijayan et al., 2003; Vodopivec et al., 2005).

PHILATELIC APPLICATIONS OF PIXE: A REVIEW

The first published report on the application of PIXE in philately was written by the late chemist and philatelist Herbert J. Almquist, appearing in the *American Philatelist* in 1985 (Almquist, 1985). Almquist worked with physicists and document experts at the Crocker Nuclear Laboratory[2] of the University of California-Davis, utilizing PIXE to analyze variations in color from blue-green to dull green of ledger lines on the paper of the Mexican "Large Numerals" stamps printed in 1887 (Scott[3] 195–211) (Figure 1).

No significant variations were found in the elemental chemistry of the different colored lines, and Almquist (1985:242) concluded "the grey-green color is derived from the turquoise-green by aging and sulfurization over a period of many years." The PIXE analyses did, however, shed light on the compositions of the paper and the ledger line ink, suggesting that clay and a calcium compound were added to the paper and that the ink was an "iron blue" compound with zinc oxide added as a whitener.

Additional analyses of the papers, as well as the ink used to print the Mexico 1-centavo green stamp (Scott 201) (Figure 2), were reported a year later in *Mexicana,* the quarterly journal of the Mexico-Elmhurst Philatelic Society International (Almquist, 1986). Almquist (1986:207) concluded that "the amounts of clay corresponding to these elements could be several percents of the paper," that the green ink and the green lines on the paper were derived from different materials, that the green color of the ink could have been derived in part from green chromic oxide, and that zinc and lead oxides were used as whiteners in the inks. A final set of PIXE analyses reported by Almquist (1988) examined the compositions of the paper used for the "Numerals" issue and three other watermarked papers used for contemporary Mexican stamps (Scott Mexico watermark numbers 152–154). The presence of relatively high amounts of magnesium, silicon, and aluminum in the Numerals paper, but not the watermarked papers, suggested to Almquist that the ledger-lined papers of the Numerals were grass based with clay fillers, while the watermarked papers were derived from wood fiber.

The first reports in the scientific literature referring to PIXE analysis of stamps were published by Johansen et al. (1986) in a report also providing "proof of concept" of PIXE's application to the forensic analysis of art objects, jewelry, and artifacts. Various examples of the Swedish "6-ore ringtyp" stamps issued in 1872 (Scott 20) (Figure 3), which exist in various shades of violet, lilac, and mauve, were analyzed in a Swedish nuclear research center, with the inked paper in the center of the stamp

FIGURE 1. The Mexican "Large Numerals" stamps of 1887. Courtesy of the Smithsonian National Postal Museum.

FIGURE 2. The 1-centavo green "Large Numerals" stamp. Courtesy of the Smithsonian National Postal Museum.

FIGURE 3. The Swedish 6-ore "ringtyp" stamp of 1872. Courtesy of the Smithsonian National Postal Museum.

evaluated separately from the inkless edges of the stamps near the perforations.

The analysis of the edges provided an assumed contribution from the paper alone. The authors determined that the inks appeared to be made from iron-and-lead- or mercury-based pigments, with zinc oxide added as a whitener. Johansen et al. (1986:48) concluded that "different proportions of the pigments give rise to many nuances, towards red and blue, and a visual classification is not easy. An objective classification can be obtained by measuring the metal content and plotting the results in a suitable way." In their summary, Johansen et al. (1986:45) reported "for one group of stamps clustering of the visually determined nuances occurred in a two-dimensional plot of lead versus zinc, while for another group a plot of mercury versus zinc showed no such clustering."

Peisach (1986), a South African scientist, in the same journal issue, was the first investigator to apply PIXE to investigate differences between genuine stamps and forgeries. Known forgeries were compared with genuine stamps from the nineteenth-century South African Republic and South-West Africa, and on the basis of multielemental analytical data, the forgeries were shown to have different compositions from the genuine stamps.

Hall and Lee (1990) published the first scientific paper specifically limited to PIXE analysis of postage stamps, in which the different chemical compositions of paper and ink were compared. In their work, several stamps from the short-lived Taiwanese republic of 1895 (Stanley Gibbons numbers 4–6) (Jeffries, 2011) were irradiated in a 4.0 MeV external proton beam. Hall and Lee (1990:573) summarized their results by stating,

> the paper and printing inks were compared between stamps made from different dies. The elemental analysis revealed that the 4 dies of stamps were printed on only 3 different types of paper. A majority of the elements observed in the stamps were printed on only 3 different types of paper. A majority of the elements observed in the stamps were due to contributions from the paper except for the red stamps which were due to cinnabar (HgS). In addition, the elemental concentrations were different in counterfeit stamps as compared to the genuine stamps.

PIXE was utilized in China by Cheng et al. (1996, 1998) to determine the ink composition of modern Chinese stamps and their reprints. They compared three stamps issued in 1950 by the People's Republic of China (Scott 57–59) with their official reprints (Scott 57r–59r), in the same color, design, and printing technique, stated by the authors to have been issued in 1995 (Figure 4).

Although the colors are quite similar to the original issues, the 1995 reprints were shown to have much different elemental concentrations and/or compositions. For example, the brown stamp (Scott numbers 57 and 57r) contains lead and zinc in the original printing, which was not present in the 1995 reprints. The relative amount of calcium was eight times greater in the reprints than in the early printings. Cheng et al. (1998:900) concluded that "we still do not know the reason for modifying the printing ink for the new edition. Maybe the original type of printing ink was no longer available due to technical improvements. However, the PIXE method can be used to distinguish between the (original printing) and (reprints) of stamps."

FIGURE 4. The Chinese 400-yuan brown "Defend World Peace" stamp (left) originally issued in 1950 and (right) later reprinted. Original courtesy of the Smithsonian National Postal Museum. Reprint courtesy of the author.

More recently, a group of Iranian scientists (Oliaiy et al., 2009) used (in conjunction with other techniques) a PIXE microprobe (which uses a micrometer-scale proton beam) scanned over a square with dimensions of 2.5 mm on each side to analyze various areas of ink and paper on eighteen Iranian stamps issued between 1881 and 1915 and printed in Austria, France, the Netherlands, and Iran. The micro-PIXE was able to indicate the characteristic elements used for inks of different colors, as well as differences in the formulas for philatelic inks of the same colors utilized in different countries. Oliaiy et al. (2009) showed a titanium compound had been added to the paper used in the Austrian-printed stamps—iron and sulfur contents of green ink were different between the Austrian-printed and French-printed stamps. There were differences in chromium and lead levels in orange inks of the Iranian-printed and Netherlands-printed examples, as well as other differences in brown, black, grey, violet, and silver inks of stamps printed in different countries, suggesting (from lack of detected metal in some colors) that certain inks were organic in nature.

Voltr and Nejedly (2012) used PIXE to analyze two early spurious Czechoslovakian stamps with double overprints on Austrian stamps from 1919 depicting Emperor Franz Joseph (Figure 5) and a 1920 Eastern Silesia stamp (Scott 5) (Figure 6), an overprint on a 20-heller green Prague Castle stamp from Czechoslovakia, to determine if genuine overprints could be distinguished from forgeries. In this case, the two Czechoslovakian stamps carried one genuine and one forged overprint on the same stamp, while two examples of the 1920 Eastern Silesia stamp were analyzed, one each with genuine and forged overprints. Voltr and Nejedly (2012:238) reported, "In all cases,

FIGURE 5. The 1919 Czechoslovakian double overprint on Emperor Franz Joseph stamp.

FIGURE 6. The 1920 Eastern Silesia stamp with overprint on Czechoslovakia 20-heller green Prague Castle stamp. Courtesy of the Smithsonian National Postal Museum.

we found barium as the most prominent element, with concentrations one or two orders higher than that of other elements” and also discovered “a specific and interesting variation of lead concentrations.”

In the Czechoslovakian double overprints, lead and iron levels “were several times higher on genuine overprint than on other places” (Voltr and Nejedly, 2012:238). For the Eastern Silesia stamp, there was a significant difference in the quantity of iron between the genuine and forged overprints, some variation in the concentrations of lead, and a much higher quantity of potassium in the genuine overprint. Voltr and Nejedly (2012:239) concluded,

> We are proposing a hypothesis that the stamping dies used shortly after the World War I were made from a material different from the one later used for falsification and that traces of the material remained in the overprints. Falsifier aimed to emulate the properties of the ink but failed to match the composition of the stamping die. As another hypothesis, we attribute the difference in potassium to the distinct printing houses—stamps A and B were originally overprinted in the printing house A. Haase in Prague in 1919, and stamp C was overprinted in Unie Praha later on.

Even with careful precautions made in Voltr and Nejedly’s experimental setup, the stamps began to show radiation damage (discoloration of the irradiated areas) after analysis, forestalling any opportunity for further examination.

CASE STUDY: PIXE ANALYSIS OF COLOR VARIATIONS IN THE 15-CENTAVO MEXICAN “MULITAS” STAMPS

The late philatelist Herbert J. Almquist had noted that color variations were known, ranging from bluish green (believed to be from the earlier printings) to greenish blue (believed to be from later printings), on the 15-centavo “Mulitas” stamp (so named because it depicts a stagecoach drawn by mules) of the Mail Transportation stamp set printed by Mexico from 1895 to 1898 (Scott numbers 251, 263, 275, and 286) (Figure 7) (Almquist, 1985).

FIGURE 7. The Mexican 15-centavo “Mulitas” stamps of 1895–1898, showing range of color variation, bluish shade on left and greenish shade on right. Courtesy of the Smithsonian National Postal Museum.

Almquist expected that the ink used to print these stamps was the same one used to print the 1-centavo green Numeral stamp (Almquist, 1988) (Figure 2). Some investigations had been made of variations in the paper of the Mail Transportation stamps (Schimmer and Bulak, 1972) but not of their ink. PIXE was an ideal technique to determine whether these variations were due to chemical differences.

Approximately 100 "Mulitas" stamps for sale from commercial stamp dealers were examined. Four stamps, each displaying the most distinctly bluish and greenish color shades, were chosen for testing. Proton-induced X-ray emission analyses were performed at the Crocker Nuclear Laboratory at the University of California-Davis (UCD) with an external beam (in air) PIXE proton milliprobe, as had been done in Almquist's analyses of the "Numerals" stamps (Almquist, 1985). This external beam PIXE analytical setup had been used for a large number of archaeometric analyses of papers and inks, including Gutenberg's Bibles (Schwab et al., 1983) and the Vinland map (Cahill et al., 1987), as well as the philatelic works of Almquist (1985, 1986, 1988). The 193-cm isochronous cyclotron at UCD produced a beam of protons with energy of 4.5 MeV, which was taken into approximately 3 cm of air, passed into the stamps generating characteristic X-rays, and collected in a Faraday cup. The beam size was a rectangle 1.0 × 0.5 mm for these analyses and was aligned by a laser to irradiate specific spots on the sample for 100 seconds. Prior analyses of historical papers and inks analyzed in this laboratory under the same setup 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. A lithium-drifted silicon energy–dispersive detector (SiLi detector) was placed several centimeters from the sample, presenting a large solid angle for X-ray detection and measurement. X-rays from the sample were counted at rates of approximately 700–1500 per second for the samples analyzed here. A thin film multielemental standard material from the National Institute of Standards and Technology was also analyzed during the run to ensure that reported concentrations were accurate and traceable. A dark area of solid ink near the top frame of each stamp of the four greenish and bluish stamps (away from any cancellation mark) was analyzed, as well as a portion of the unprinted, uncanceled paper in the top margin of all eight stamps.

Only eight chemical elements were detected in the ink and paper of the stamps. Three elements were present at relatively high densities, exceeding a microgram per square centimeter: zinc, silicon, and sulfur. Five "trace" elements were detected at lower concentrations: lead, calcium, iron, titanium, and chlorine. Distinct differences in elemental composition between bluish and greenish inks of the "Mulitas" were noted, as were differences between the "Mulitas" inks and papers and those of the "numerals" analyzed by Almquist (1986, 1988) using the same machine and experimental setup.

Unlike the "Numerals" stamps (Figure 1) previously analyzed by Almquist (1985, 1986, 1988), which were apparently printed with potassium-and iron-based, chromium-bearing inks on papers with clay (magnesium, silicon, aluminum, and calcium) coatings or fillers, the absence or much lower concentrations of these elements in the "Mulitas" stamps suggests they may have been printed with organic-based inks on papers largely devoid of clay fillers. This and the presence of sulfur suggests that Mexican stamps could have been printed with aniline (sulfone-derived organic) pigments earlier than 1899, as had been previously thought (Schimmer and Bulak, 1972). The "Mulitas" paper is harder and stronger than the "Numerals" paper, which was easily torn, perhaps due to the latter's clay- and calcium-based fillers. The "Mulitas" paper is noticeably lower in calcium than other eighteenth-century papers investigated in prior PIXE analyses (Cahill et al., 1981).

Oxides or hydroxides of zinc, lead, and/or titanium were often added to Mexican (Almquist, 1985, 1986) and other (Johanson et al., 1986; Hall and Lee, 1990; Voltr and Nejedly, 2012) postage stamp inks of the late nineteenth century as brighteners, lighteners, or extenders. The presence of these elements in the "Mulitas" inks, along with their relative scarcity in the paper, suggests they were modulated color shades of the "Mulitas" stamps, with bluish inks having more zinc and lead and less titanium and greenish inks having less zinc and lead and more titanium. These elements could have either directly influenced the shade of the ink as printed or secondarily protected against a postprinting color change of the stamps potentially caused by the sulfur in the inks.

CONCLUSIONS

Proton-induced X-ray emission spectrometry has been a useful technique for the analysis of philatelic inks and papers for more than 30 years. Although the machines required to perform a PIXE analysis are relatively few and not commercially available, when this method can be utilized, its ability to determine low concentrations of metals, for example, in organic-based inks and papers, keeps it relevant. PIXE analysis has shown that a widely used practice controlling color shades of nineteenth-century stamp inks was the addition of metal oxides as whiteners. In addition, the papers used to print stamps of that era from many entities contained clay mineral elements as fillers. PIXE also has shown utility as a forensic tool, through its ability to discriminate chemical differences between original, genuine stamps and forgeries or reprints.

The case study of the 1895–1898 Mexican "Mulitas" stamps indicated that they, unlike the previous Mexican issues, were printed with organic-based inks on largely clay-free papers. Mexican stamps appear to have been printed with organic inks several years earlier than previously believed. Differing amounts and/or formulations of metal (Zn, Pb, and 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.

PIXE is one of many tools described at the First International Symposium on Analytical Methods in Philately that have been used for philatelic analyses. Since PIXE is an elemental analysis technique, it may be combined with other techniques determining the actual chemical compounds or molecules for a more complete nondestructive analysis. In conjunction with PIXE or XRF elemental analyses, other methods that have been successfully applied to stamps, such as Fourier transform infrared spectroscopy (Poslusny and Daugherty, 1988; Ferrer and Vila, 2006), Raman spectroscopy (Castro et al., 2008; Jelovica Badovinac et al., 2010; Withnall et al., 2012), and/or X-ray diffraction (Foner and Adan, 1983; Liston, 2005; Vila et al., 2007; Lera et al., this volume; Brittain, this volume) should be able to discern the specific component compounds of the ink and paper.

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NOTES

1. When the Vinland map, supposedly a fifteenth-century map of the Earth, was analyzed by PIXE, titanium was found to be a component of the ink; other analytical techniques suggested that the titanium was in the form of the compound anatase, a material not synthesized in such a form until the twentieth century.

2. The Crocker Nuclear Laboratory at the University of California-Davis, one of the first institutes where PIXE was used for analysis of historical inks and papers, was named after University of California Regent William Henry Crocker (1861–1937), who not only funded one of the first cyclotrons in the university system but also was a philatelist and one of the 100 founding members of the Collectors Club of New York.

3. All references herein to "Scott" refer to the catalogue numbers and, where specified, watermark numbers, assigned in the *Scott Standard Postage Stamp Catalogues*, published every year by Scott Publishing Co., Sidney, Ohio.

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Statistical Estimates of Rare Stamp Populations

David L. Herendeen and Gary C. White

ABSTRACT. This paper describes a statistical method for estimating the population of rare stamps from auction catalogs, price lists, expert certificates, and other generally available records. The method presented was developed by biologists to estimate animal populations. Such estimates are done by first capturing, marking, and releasing specimens and then recapturing them. From these data, statistics may be developed to estimate the total population. The latest-generation computer software used for such analyses, called MARK, was developed by Gary C. White and others at Colorado State University. This paper explains how MARK may be used by everyday philatelists interested in estimating the number of rare or very scarce stamps or covers in their collecting area. The methods described do not require one to be a mathematician to use them successfully. The methodology is then applied to four test cases in order to illustrate the efficacy of the approach.

PHILATELIC BACKGROUND

One of the most difficult tasks facing the stamp collector, researcher, and exhibitor is determining the rarity of particular stamps, whether alone or on cover. This is important for exhibitors because it allows them to make claims as to the rarity of items in their collections in a quantitative manner. This is usually done with statements such as "number reported," "number recorded," "number seen by the exhibitor," or, most important, number according to a recognized expert or group of experts with published results. Generally, such numbers are based on censuses conducted by a specialist, or groups of specialists, often over prolonged periods of time.

However, experience has shown no matter how well a census is done, just as with the U.S. population census, not every item that exists will be included, and other individuals will subsequently come to light. Consider, for example, Alexander's monumental work (Alexander, 2001), in which he identified and counted the covers franked with either or both of the first two U.S. stamps (Scott 1 and 2)[1] owned by more than a hundred collectors over 25 years (Scott Publishing Co., 2012a, 2012b). This census resulted in a count of nearly 13,000 covers at the time of publication. A recent update to this census (Scheuer, 2012) shows at least 1,300 new examples that have been identified in the intervening years.

Since it is neither practical nor possible to exactly count any given stamp population, perhaps a method that can provide a statistically valid quantitative estimator can be developed by transferring an existing technology to the philatelic domain. That is the intent of this paper.

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STATISTICAL BACKGROUND

A branch of statistics that originated in the field of ecobiology is devoted to developing methods for estimating the population of animals in a specific geographical area. Such techniques, whose origins can be traced to the 1930s, are commonly called capture-recapture methods. For interested readers, the historical background is summarized in White et al. (1982). A brief overview of these methods, intended to address the average philatelist, is presented in the following sections.

The Capture-Recapture Model

The basic premise of this statistical methodology is that by trapping animals and marking them, one can recapture them at a later time and by simply counting the number of recaptured animals can estimate the total size of the animal population. Two important assumptions must hold. The first must be the population is closed, that is, there are no births or deaths (demographic closure), and the second must be there is no movement in or out of the area (geographic closure).

As a simple example, suppose that one wants to estimate the number of rabbits in Sherwood Forest. A number of rabbit traps are set throughout the forest. The traps are checked the next morning. The traps were successful in capturing $n_1 = 32$ rabbits. Each rabbit is then identified with, perhaps, an earmark and released. The traps are then taken away. One week later, the traps are reset. This time, $n_2 = 50$ rabbits are captured. But only one of these was earmarked ($r_2 = 1$). Assuming that the probability of trapping any specific rabbit is equal to that of any other rabbit, the chances of capturing a marked rabbit may be estimated by

$$\frac{r_2}{n_1} = \frac{n_2}{N} = \frac{1}{32}.$$

It is possible to make a simple estimate of the total population,, using the Lincoln-Petersen estimator (Cooch and White, 2012). The result is

$$\hat{N} = \frac{n_1 n_2}{r_2} = \frac{32 \quad 50}{1} = 1{,}600.$$

This is the general idea, but as one may expect, the real problem is not so simple.

Program Mark

Colorado State University has been at the forefront of research in this area since the 1970s. White and others have developed several generations of computer software designed to solve this problem using various levels of complexity. This research has led to the program MARK (http://warnercnr.colostate.edu/~gwhite/mark/), which embodies the majority of proven methods for solving capture-recapture problems (White et al., 1982; White and Burnham, 1999).

As will be discussed later in this paper, the methods most usable to estimate rare stamp populations are those that assume a closed population. As noted earlier, this simply means that there is a stable population: no births or deaths and no immigration or emigration. Readers might observe that there may be several instances of "death" in a stamp population. This would include copies destroyed by mishandling or war, copies that "mysteriously" disappear, and copies that find their way into museum collections. This will be discussed in the next section. Also, there is no movement in or out of the area being sampled. As will be seen, this assumption is always met for the philatelic application.

Program MARK has a number of models for closed population analyses. There are four possible model combinations that consider different population dynamics of animals, but do they have application to stamps?

The four models, first proposed by Otis et al. (1978), are as follows:

- M_0: In this simplest model, it is assumed the probabilities of capture and recapture are constant. This means there is no difference in the chances of capturing or recapturing a specific animal on any occasion.
- M_t: This model allows for a variation of capture and recapture probabilities as a function of time. Each animal may have a different capture probability for different times, but these probabilities will be constant for all animals for each trapping occasion.
- M_b: This model allows for the behavior of specific animals to affect their probability of capture. For example, there are some animals that might enjoy the trapping (trap happy) and those that do not (trap shy). However, the initial capture probability is the same across time. Further, this model works by seeing a decline in the number of new animals captured on succeeding occasions; that is, there is a depletion of animals. When such a decline is not happening, then the result is an unidentifiable estimate.
- M_h: This model considers the heterogeneity of the population. Heterogeneity in this context means the capture probability is different for each animal, but there is no variation across time.

Beyond these models, it is also possible to consider these different factors (M_t, M_b, and M_h) in pairs (e.g., M_{tb}) or even taking all three possibilities simultaneously, resulting in M_{tbh}. Some of these combinations result from the work of other researchers, but a detailed list of these is not necessary for this paper.

The most interesting question is which of the four possible models most accurately reflects a rare stamp population? As will be seen, the estimation of rare stamp populations is quite similar to the animal population estimate. Since the stamps are neither sentient nor able to learn, there can be no behavioral differences.

THE STATISTICAL ASSUMPTIONS

The typical capture-recapture algorithms have broad applicability, but the single assumption that greatly simplifies their application to the stamp estimation problem is the population is closed. While it is true stamps may be lost or destroyed over time, this is usually negligible. On the other hand, it is possible that a large percentage of very rare stamps may be "lost" to museums. Is it necessary to consider this? Yes, it should be considered, and the easiest way to model this is to simply remove such stamps from the study and then add them back into the results. For example, suppose four of ten copies of a rare stamp are in museums. Then an analysis is performed for the other six stamps. Assume the model estimates that there is a population of eight stamps. Then we add the four museum copies (which are known to exist) to the estimate, arriving at 12 stamps (8 + 4).

In order to use the MARK program successfully, there are other necessary assumptions, which, for our problem, are as follows:

- Individual stamps maintain their identification over time. That is, one can always identify a given sample from its perforations, centering, cancel, or context (as on a cover). This is easily met for truly scarce stamps.
- All of the stamps are correctly identified when they appear in an auction, price list, or other public forum. Since we are dealing with rare items, we may assume photographs or scans are always available. If not, the occurrence is ignored.
- Each stamp has a constant and equal probability of being sold during a given capture period. Gates (1991) asserted this assumption may be violated because strong upward price pressure may cause more of the stamps to "come out of hiding." The first author feels that most of the philatelic rarities are not purchased for investment but are rather purchased by dedicated collectors and exhibitors who intend to hold them for long periods.

As an example, the mean holding period for the Labuan stamps, discussed later in this paper, has been more than 24 years. This is real dedication.

SELECTING TEST CASES

In order to test the hypothesis that MARK could be used as an important philatelic tool, a number of test cases were selected and executed and the results were analyzed. To this end, four sample problems were chosen. These analyses were all based on earlier detailed census keeping by various researchers. They have been selected to incorporate a number of different characteristics. The test cases are described below.

- The first test case considers one of the most spectacular errors in U.S. philately: the 24¢ inverted "Jenny" airmail stamp issued in 1918 (Scott C3a). This case is important because the population of these iconic stamps is precisely known.
- The second test case uses the census and provenance data for the 8¢ Labuan inverted frame postage due stamp (Scott J6a) performed by Herendeen (2006). This case provides two sets of data, the census through 2005 and then the extension of the census to 2011. Together, these allow the predictive capability of MARK to be examined.
- The third is based on the detailed records of Hawaiian stamps and covers maintained by Gregory (2012). Specifically, the data used relate to the 5¢ provisional overprint issued in 1853 (Scott 7). This case checks that the estimator works as well for covers as for stamps.
- The fourth example studies a scarce U.S. stamp, the data for which were provided by the Robert A. Siegel Auction Galleries, Inc. Web site. This stamp is the U.S. 1¢ stamp made from coil waste and issued from 1923 to 1926 (Scott 594). Only the used stamps were considered for this study. This case checks results for a less precise data set that has many observations based on expert certificates in addition to auctions. With 488 observations, this is also the largest set of the test data.

If all of these test cases result in reasonable estimates that correlate well with reality, then it may be concluded that MARK will be useful to philatelists.

ASSEMBLING THE DATA

Several steps must be taken to gather the input data for the statistical model. These include acquiring the raw data describing the encounters with specific stamps or covers. The data are then divided into time intervals for analysis. These procedures are described in this section.

Raw Data Acquisition

While often laborious, the assembly of raw data needed to perform the statistical analysis is easily done. Using any application software that allows you to enter and sort data (such as Microsoft Excel), you simply record each appearance of the stamp or cover under consideration. Data sources may include auction catalogues, retail price lists, copies of expert certificates, and any other similar records. It is most important that all the items are illustrated to allow positive identification.

In theory, only two pieces of data are required for each observation, but for completeness, three are recommended as a minimum. In fact, the collector may wish to include many different data items so that retracing this step will never be necessary. The minimal items are as follows:

- The sample identifier. A unique number, or other string of characters, which is assigned to each stamp or cover identified.
- The location where the sample was captured. This could be an auction catalog, price list, expertizing certificate, or any other reliable source.
- The date the sample was seen, offered, or sold. Full dates are preferable for completeness, but just the year is usually sufficient.

Examples of these data are seen in Table 1 for the Labuan inverted frame postage-due stamp.

Selecting the Time Interval

Once the basic data have been assembled, the number of time intervals representing sampling occasions must be selected. This is especially important with rare stamps because the data are much sparser than for the typical animal populations.

In a subsequent section, the results of the statistical analyses for different time steps are presented. It appears from these results that no great variations in solutions occur (i.e., less than a 10% variation). Therefore, the best estimates should probably be those obtained from using a one-year time interval as the "encounter occasions."

APPLYING THE STATISTICAL MODEL

Once the data are assembled, they are entered into an Excel spreadsheet. Then, special software, called POPULATION, is used to generate the data for MARK. This software has been developed by the Institute for Analytical Philately, Inc. (IAP).[2] MARK is then executed and the results are produced. This process is described in the following sections.

MARK Input

The MARK program input is a computer text file that has a Windows file extension of .INP. While it is possible to create such files manually, IAP's software tool POPULATION[3] provides a special utility for use with philatelic data. Instead of creating the .INP file manually, the user creates a Microsoft Excel spreadsheet containing the raw survey data.

A partial history of the Labuan inverted frame postage-due data is shown in Table 1. It contains a unique sample number for each of the stamps seen, the "trap," which is the source of the data, an unused column labeled "year," and the exact date that the stamp was seen.

As will be seen in Herendeen (2012) (hereinafter the *Users Guide*), there are many different options available within POPULATION. For example, when executed, POPULATION converts the exact dates into the years for further processing. The user might have just as easily entered only the years into the spreadsheet.

POPULATION is then executed. The output is simply the MARK .INP file. An extract of this file is shown in Table 2. Again, a detailed description of the meaning of this data may be found in the *Users Guide*.

MARK Output

After preparing the input data, the MARK program is executed. Step-by-step details are found in the *Users Guide*. The results of MARK are the statistical computation of the stamp

TABLE 1. The history of the 8¢ Labuan inverted frame postage due stamp.

Sample	"Trap"	Date
1	Paris	1 May 1907
12	Royal Collection	1 Jan 1920
13	Ferrary	26 Apr 1923
17	Harmer-UK	14 Mar 1932
21	Harmer-UK	23 Mar 1935
27	Harmer-UK	16 Dec 1935
28	Harmer-UK	16 Dec 1935
15	BPA	1 Jan 1936
31	RPSL	1 Jan 1936
18	Harmer Rooke	1 Dec 1937
26	Harmer-UK	10 Oct 1938
14	Klein	21 Feb 1939
7	Harmer-UK	21 Oct 1947
7	Harmer-UK	25 Oct 1949
13	Harmer-UK	10 Jan 1950
3	Harmer	14 Nov 1950
22	Friedl	9 May 1951
10	Harmer-NY	9 Apr 1957
5	Harmer-NY	30 Sep 1958
9	Corinphila	18 Nov 1959
29	Siegel	24 Feb 1966
21	Gibbons	13 Feb 1969
1	Robson Lowe	30 Jun 1971
18	Harmer-NY	25 Feb 1975
6	Harmer-NY	17 Oct 1979
24	Harmer-NY	25 Mar 1981
27	BPA	1 May 1981
2	Gibbons	4 Mar 1982
3	Sotheby	6 Sep 1984
16	Christies	23 Oct 1984
32	RPSL	1 Jan 1989
5	Manning	19 Nov 1989
13	Siegel	1 May 1990
13	Western	8 Dec 1990
3	Shreve	7 Nov 1991
8	Robson Lowe	17 Dec 1991
16	Christies	5 Mar 1992
18	Shreve	23 May 1992
5	Holtz	1 Apr 1993
22	BPA	1 Jun 1993
4	Cherrystone	9 Aug 1993
25	RPSL	1 Jan 1994
19	Christies	9 Mar 1994
3	BPA	1 Feb 1995
19	Harmer-UK	18 Dec 1996
1	RPSL	1 Jan 1997
10	Ivy-Mader	1 Jun 1997
17	BPA	1 May 1999
23	Gibbons	15 Oct 1999
9	Singer	1 May 2000
21	Spink	23 Jun 2001
17	Bennett	24 Jun 2001
19	Spink	23 Feb 2003
20	Spink	21 Jun 2003
15	Dealer Stock	1 Jul 2003
19	Dealer Stock	1 Jul 2003
11	BPA	1 Aug 2003
25	Spink	16 Oct 2003
9	BPA	1 Nov 2003
15	Grosvenor	19 Nov 2003
30	Roumet	27 Jan 2004
33	Brun	1 Jan 2005
28	Victoria	7 May 2005

TABLE 2. Extract from MARK data created from Excel spreadsheet.

```
/* Labuan invert  through 2005,  annual encounters */
/* Number Occurrences = 99:  Starting in 1907 ending in 2005 */

/* 1:3 */ 100000000000000000000000000000000000000000000000000000000000000010000000000000000000000000100000000 1 ;
/* 2:1 */ 000000000000000000000000000000000000000000000000000000000000000000000000000100000000000000000000000 1 ;
/* 3:4 */ 000000000000000000000000000000000000000000010000000000000000000000000000000000000100000010001000000000 1 ;
/* 4:1 */ 000000000000000000000000000000000000000000000000000000000000000000000000000000000000001000000000000 1 ;
/* 5:3 */ 000000000000000000000000000000000000000000000000000100000000000000000000000000000010001000000000000 1 ;
…
…
/* 29:1 */ 000000000000000000000000000000000000000000000000000000000001000000000000000000000000000000000000000 1 ;
/* 30:1 */ 000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000010 1 ;
/* 31:1 */ 000000000000000000000000000001000000000000000000000000000000000000000000000000000000000000000000000 1 ;
/* 32:1 */ 000000000000000000000000000000000000000000000000000000000000000000000000000000000010000000000000000 1 ;
/* 33:1 */ 000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000001 1 ;
/* Number Observed = 33 */
```

TABLE 3. Typical output from program MARK.

	Labuan 99 sampling occasions Real function parameters of {closed capture}			
			95% confidence interval	
Parameter	Estimate	Standard error	Lower	Upper
1:p	0.0139593	0.0024567	0.0098795	0.0196905
2:N	43.416165	5.2347971	37.109245	59.403024

population as well as other statistical estimates. A sample output is shown in Table 3, which provides the summary of the statistical quantities estimated.

For this simple model, these are *p*, the probability of capture or recapture for all of the stamps on each occasion, and *N*, the estimate for the total stamp population. These statistics include the estimate of each parameter and the lower and upper bounds of the 95% confidence interval for the estimates. This can be interpreted as the probability of the true answer lying between the lower and upper bound being 95% (although the actual statistical description is more complex).

EXPERIMENTAL VALIDATION

To test the applicability for philatelic analysis of the statistical models used by MARK, four sample problems were assembled. These test cases, along with the purpose for each, were described in an earlier section. The results of these cases follow.

The Inverted Jenny—A Closed-Form Comparison: Test Case C3a

A single sheet of 100 of the U.S. 24¢ "Jenny" airmail stamp was printed in 1918 with the center inverted, as seen in Figure 1 (Scott C3a).

Amick (1986) presents a very detailed study of the appearances of all 96 of the recorded examples and recounts the details of this fascinating discovery and the many intrigues associated with it. No information about the missing four stamps has appeared since the initial dispersal of the stamps.

This test case is particularly interesting for two reasons. First, it allows the fidelity of the MARK program to be determined relative to an exact population size known a priori, and second, this problem was solved in the philatelic setting (Gates, 1992) using an earlier generation of capture-recapture software called CAPTURE (White et al., 1978).

The Amick (1986) data were processed using POPULATION, and the results were used as input to the MARK program.

FIGURE 1. The “inverted Jenny” of 1918. Courtesy Smithsonian National Postal Museum.

FIGURE 2. The Labuan inverted frame postage-due stamp. Courtesy of the Smithsonian National Postal Museum.

TABLE 4. Comparison of statistics for the inverted “Jenny” population.

		95% Confidence Interval	
Study	**Estimate**	**Lower**	**Upper**
MARK	96	96	102
CAPTURE (Gates, 1992)	107	94	121

In the 62 years between 1925 and 1986, there were 427 observations of this stamp. The “closed capture” model was used, and it was assumed that the probabilities of both capture and recapture were equal for all 96 stamps. MARK then found a solution. The results, along with those of Gates (1992), are shown in Table 4.

It is noted that the MARK results are of very high fidelity and predict that there are 96 examples. The upper bound of the 95% confidence interval estimates 102 stamps. The much less precise results from CAPTURE occur simply because the older software had more limitations, especially in the number of occurrences allowed. As a result, Gates (1992) had to make certain assumptions that resulted in much greater variations from the known number of stamps.

The results shown in Table 4 indicate the methodology embodied in MARK is well suited to solving the philatelic population problem. For the remainder of the paper, the notation “[lower CI,prediction,upper CI]” will be used to express the statistics. Thus, the results shown in Table 4 may be stated as

MARK: [96,96,102]
CAPTURE: [94,107,121].

The Labuan Postage-Due: Test Cases Labxx

The Herendeen (2006) study identified 33 examples of a variety of the postage-due stamps issued by the British colony of Labuan in 1901 (Scott J6a). These stamps are especially rare because, as shown in Figure 2, they exhibit the inverted frame error. Unlike the inverted airmail stamp discussed above, these stamps were separated into singles prior to sale. They were also canceled to order[4] at the point of sale with a seven-bar elliptical obliterator. The first recorded public appearance was in 1907 at an exhibition in Paris. The study found 63 reported instances of these stamps from 1997 through 2005, whether appearing in public auctions, submitted to expertizing organizations, or found in dealers’ stock. There are undoubtedly other appearances not uncovered during the study. Interestingly, the MARK algorithms are known to be unbiased by the fact that some data are missing.

The 63 observations in 99 years represent a very sparse set of data in the statistical sense. If, for example, the statistical model assumes 99 one-year “trapping periods,” then only 42 of these periods result in finding a “trapped” stamp.

To determine whether the discretization of time plays an important role in the statistical analysis, three cases were run:

- 10-year time steps (10 occasions),
- 5-year time steps (20 occasions), and
- 1-year time steps (99 occasions).

Table 5 compares the results of these three models. There is no meaningful difference between them, with the population

TABLE 5. Comparison of statistics for three different sampling intervals.

			95% confidence interval	
Test case	**Estimate**	**Standard error**	**Lower**	**Upper**
LAB10	44	5.71	37	62
LAB20	46	6.26	38	65
LAB99	43	5.23	37	59

FIGURE 3. Cover showing the use of the Hawaiian 5¢ provisional overprint, Scott 7. Courtesy of the Fred Gregory Collection.

estimate varying from 43 to 46 and the 95% confidence intervals varying from 37 to 65. Thus, the sensitivity of the solution to the time discretization is small. However, since the execution time of the MARK program is so fast for the philatelic application, the first author feels it is easier to simply model the data on an annual basis.

As will be seen in a subsequent section of this paper, this sample problem also allowed a simulated solution for the updated basic data, which shows how the statistics can be used as a predictor.

The Hawaiian Provisional On Cover: Test Case Hawaii

The third sample problem is drawn from a Web site called Post Office in Paradise.[5] The analysis considers the scarce use of the 5¢ provisionally overprinted stamp (Scott 7) on cover as shown in Figure 3. Gregory (2012) has archived only 18 such covers encompassing 66 observations from 1909 until 1999.

A MARK input file was created from these raw data. The input matrix had 18 rows and 91 columns. The program was executed and resulted in the following estimates for [lower CI, prediction, upper CI]: [18,18,24].

The convergence of the estimate to the number observed is explained by the large number of occurrences, 91. This is interpreted to indicate that an additional five examples might be found.

The US 1914 1¢ Coil: Test Case US594

The final example analyzes the data for the U.S. 1¢ stamp made from coil waste and issued from 1923 to 1926 (Scott 594), shown in Figure 4. The Scott catalog indicates that sheets comprised either 70 or 100 stamps. Raw data were obtained from the Robert A. Siegel Auction Galleries, Inc. Web site.[6] In addition to auction records, many stamps were reported only when

FIGURE 4. Example U.S. 1¢ green, rotary, perforation 11 stamp (Scott 594). Courtesy of Robert A. Siegel Auction Galleries, Inc. Sale 976, Lot 2170, 29 September 2009.

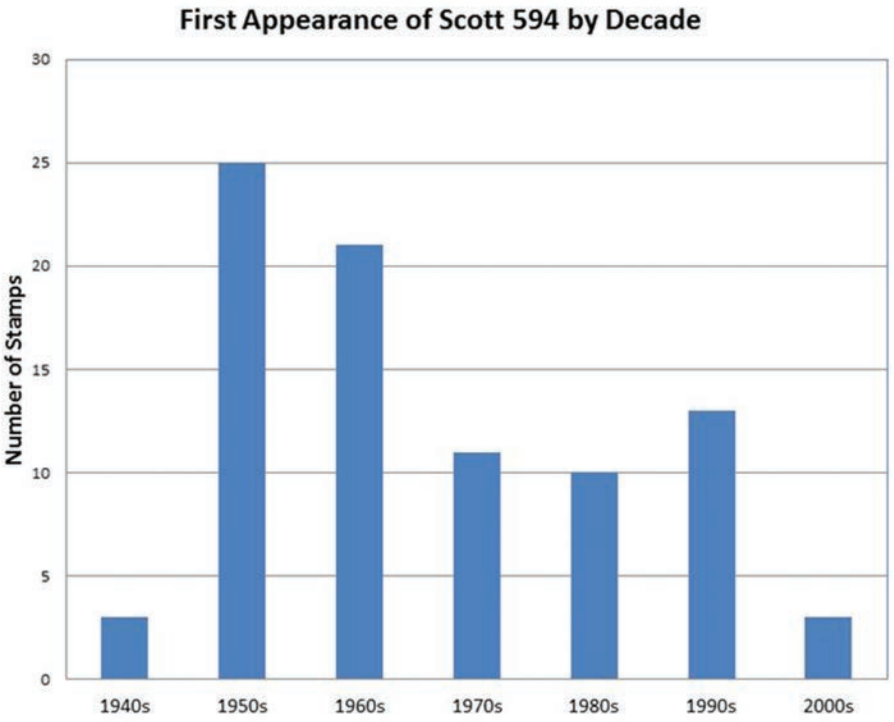

FIGURE 5. First appearance of Scott 594 by decade.

they received certificates of genuineness, most from the Philatelic Foundation.[7] These data were all used to form the observation base. Only the 88 recorded used copies of the stamp were included because they form a larger sample space than the 18 mint examples.

The total number of observations from 1940 to 2008 was 199. A MARK input file was created from these data. The input matrix had 88 rows (one for each stamp) and 69 columns (one for each year). MARK was executed, resulting in [lower CI, prediction, upper CI]: [95,101,115]

This is interpreted to indicate that there are probably another 13 stamps yet to appear and perhaps as many as 27 more stamps. Considering that at least 100, and probably more, of these stamps were printed, this is not surprising.

As an additional check, the plot shown in Figure 5 shows the frequency of appearance by decade. Three new examples appeared in the 2000s and 13 in the 1990s. There is no reason to believe that others will not appear in the coming years.

PREDICTING THE FUTURE

Four test cases have been analyzed using the MARK program. The results appear to be consistent with the actual stamp populations as measured by censuses. Now, how can these statistical estimates be used to predict what might happen in the future? Two methods can help in determining this. The first is to simulate the passage of time by incrementally analyzing a stamp and the second is to actually look at the results of a real case. These are both described in this section.

TEST CASES US594

With 199 observation of this rare stamp, the U.S. 1¢ stamp of 1923 affords the best opportunity to do a simulation of the predictive power of these statistical methods. Recall from Figure 5 that new "discoveries" have been made across the seven decades since the first reported sighting of the stamp.

A simulation will now be made assuming that this methodology had been available in 1980. This is done by simply truncating the database of observations to any given year. To that end, the statistics were computed for periods through 1980, 1990, 2000, and 2008 (the end of the available data). The results of these four analyses are shown in Figure 6. This figure shows, for each of the decades, the upper and lower bounds of the 95% confidence interval (UB 95% CI and LB 95% CI) and the estimate of the number of stamps. One of the interesting characteristics of statistical methods is the more items we see, the more we predict exist. This appears to be stabilizing during the full time range. The final estimates [95,101,115] are certainly plausible and would indicate that the number printed would be at least 140 or 200 depending on the sheet size.

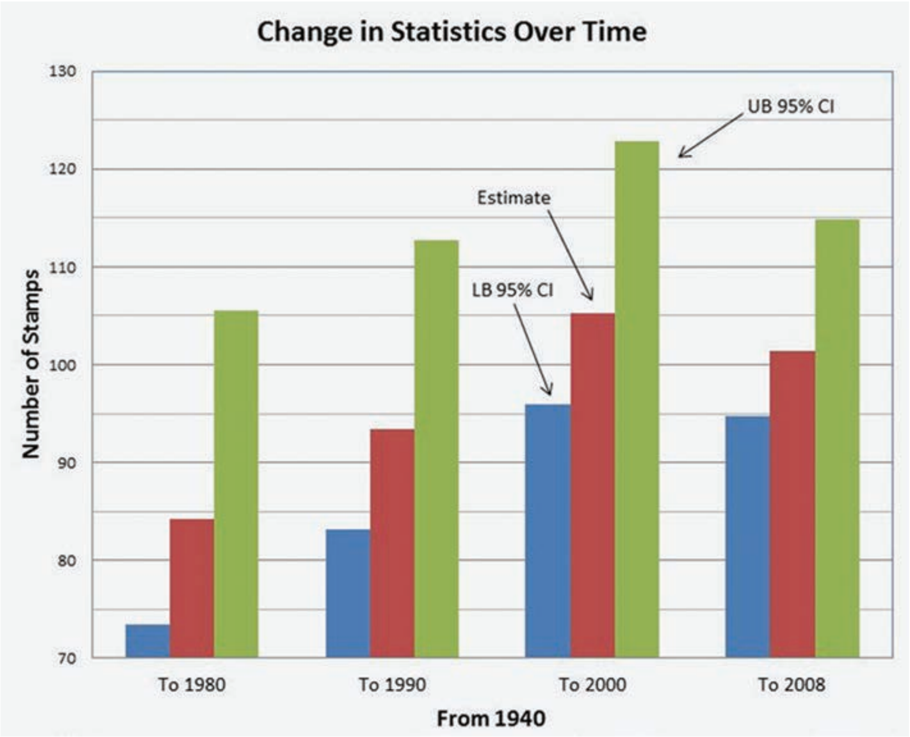

FIGURE 6. Stability of simulated MARK solutions over time for Scott 594. Blue: lower bound, red: estimate, green: upper bound.

TEST CASE LABNEW

As seen previously, the Herendeen study was published in 2006, and the data used in the study ended in 2005. The results of the MARK analysis were [36,41,54]. Therefore, although only 33 stamps were in the census, the model estimated that there would be 41 examples. What has actually happened?

In the intervening seven years, there have been 16 new observations of the Labuan inverts. Most important, four of them were not included in the 2006 census. In other words, there are now 37 known examples. Again, the more items seen, the more probably exist.

The new data were executed by MARK. The results were [40,45,57]. This shows that there is a useful predictive aspect to the statistical analyses.

ADVANCED STATISTICAL MODELS

As noted at the beginning of this paper, other models can be used to improve the estimates for populations of animals. In addition to M_0, which has been used for our sample problems, there are also M_t, M_b, and $M_{h.}$ Furthermore, these may be applied in pairs (e.g., M_{tb}), or even all three possibilities can be used simultaneously, resulting in M_{tbh}. The multiple-model approach leads to a set of models, each with an estimate of N, and hence leads to model selection and how to combine the estimates from multiple models. This is a topic for future work and is beyond the scope of the current paper.

OTHER OBSERVATIONS

Usually, statistical methods are at their best when large samples of data are available. As seen, this is generally not the case for rare stamps, where individual encounters may span decades. How can the MARK program handle situations such as<bl>

- stamps with a known upper bound or
- ultrarare stamps (<4)?

It has already been shown in test case C3A that excellent results were obtained for a stamp whose population has a known upper bound.

A simple test case was created to determine how MARK handles an ultrarare stamp of which only two examples have been seen after 150 years. The subject stamps selected were the U.S. 1¢ Z grill stamps of 1867 (Scott 85A). Again, the Robert A. Siegel Auction Galleries, Inc. maintains an online database of censuses for some rare stamps, including this one. The encounter histories for the two stamps are quite simple. The first example was sold in the mid-1920s (assume 1925) to the New York Public Library, where it remains. The second appeared in 1919, 1957, 1975, 1977, 1986, and 1998.

The input data for MARK thus included seven encounter histories from 1919 to 1998. This model was run and resulted in a population estimate of [2.0,2.0,2.0]. The statistical estimate has converged to the actual census number. This is an excellent result.

CONCLUSION

This paper has described a statistical method for estimating the number of rare stamps and covers from available records such as auction catalogs, price lists, and expertizing organizations. The basic method, well established in the field of wildlife biology and implemented in a computer program called MARK, was exercised using four philatelic test cases. In each test case, the results were completely plausible and correlated well with simulated predictions of future appearances of the rare stamps.

In addition, IAP has made available a Microsoft Excel–based application called POPULATION that allows philatelists to go from census data to input to the MARK program. IAP has also written a user's guide for philatelists to use MARK and POPULATION to get results without being a domain expert in advanced statistical analysis.

ACKNOWLEDGMENTS

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NOTES

1. Stamps in this paper are referenced by their Scott number as given in *Scott Specialized Catalogue of United States Stamps* (Scott Publishing Co., New York, 2010) or *Standard Postage Stamp Catalogue*, Volume 1, Scott Publishing Co., 2008).

2. The Institute for Analytical Philately, Inc. is a nonprofit corporation that sponsors research that develops methods for applying scientific methods to the solution of philatelic problems. For more information, see www.analyticalphilately.org.

3. The Microsoft Excel–based application POPULATION includes software to convert the simple observation data into the INP file used by MARK. The actual input data are entered into the data spreadsheet. A portion of the test case LAB data is shown in Table 1. For complete details, readers are directed to a separate document (Herendeen, 2012) that provides a comprehensive user's manual for these procedures. The PopUtil spreadsheet and manual are available from IAP by going to www.analyticalphilately.org and first selecting "Free Software," then selecting "Population" and following all of the instructions found there.

4. Canceled-to-order stamps are those that have cancellations applied before they are ever sold to the public. This allows the distributor to set a price not related to the face value of the stamps. The Labuan stamps were sold at the British North Borneo office in London.

5. The Web site www.hawaiianstamps.com, most often referred to as Post Office in Paradise, was created by and is maintained by Fred Gregory.

6. Robert A. Siegel Auction Galleries, Inc. is one of the premier auction houses for U.S. material. In addition, their Web site www.siegelauctions.com includes a number of tools and resources. One of the most important of these is census data for many rare U.S. stamps. This was the source of the raw data for the US594 test case. Stamp illustrated is census number 594-OG-11. http://www.siegelauctions.com/dynamic/census/594/594.pdf.

7. The Philatelic Foundation is the leading expertizing organization in the United States. It keeps extensive records of the stamps that have been viewed. For more information, see http://www.philatelicfoundation.org/.

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Reflectance Spectroscopy of Colored Overprints

Lyman R. Caswell

ABSTRACT. This paper describes a new methodology for analyzing overprinted stamps. This methodology is based on two procedures. The first performs precise measurements of the dimensions of overprints and a statistical analysis of the minor variations present among them. The second performs a colorimetric analysis of the ink used for printing the overprints. The goal is to determine if these methods can differentiate between overprints made by different printers and if they can allow rapid identification of counterfeit overprints. A set of overprinted stamps from post–World War I Hungary was selected for testing samples. These stamps had many varieties, were produced by two different print shops, and were often counterfeited. After describing the different scientific testing performed, this paper outlines general procedures that may be used by other researchers.

INTRODUCTION

One of the difficult tasks in philately is the scientific analysis of overprints on stamps. This observation led Souren (1939:18) to write, in reference to his expertizing organization, "However, no opinion will be advanced on surcharged stamps except as to the condition of the basic stamp. It will necessitate years of preliminary research before scientific proof of the true nature of overprints can be determined satisfactorily."

More than 70 years later, the need for methods that allow overprint identification remains extremely high. Two particularly important areas are the ability to precisely measure all overprint dimensions and the ability to determine, in a quantitative manner, the color of the ink used for the overprint. Identification of color is important in making the distinction between different printings of a given stamp design and between genuine and counterfeit printings. It can make the difference between a stamp of little value and one of great rarity.

COST-EFFECTIVE EQUIPMENT

Developments in analytical instrumentation using various forms of electromagnetic radiation permit new methods of examination and analysis of the colors and compositions of the inks of stamps. These techniques have recently been evaluated for, and used in, philatelic applications (Lera, 2012; Lera et al., this volume).

Visual color identification is subjective. It is dependent upon the age and the sex of the observer and upon the conditions of observation (Herendeen et al., 2011:106). The spectrum of the light reflected from the surface of one stamp can be compared with the spectrum of the light reflected from a second stamp to determine if the colors of the two

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stamps are the same or different (White, 1979), but this comparison does not necessarily describe the colors of the stamps as seen by the eye.

More important, the cost of analytical instruments has dropped dramatically over the last 10–20 years, allowing the proliferation of such devices and increased access to them for philatelists. This is greatly facilitated by the facilities at the Smithsonian National Postal Museum (NPM).

The VSC 6000

One of the analytical instruments available at the NPM is the Foster + Freeman, Ltd. Video Spectral Comparator (VSC 6000). This spectrophotometric device allows the quantitative measurement of color, which allows the correlation of reflectance spectra with accepted color systems (Foster + Freeman, Ltd., 2011).

The most widely accepted color systems are those established by the Commission Internationale de l'Éclairage (CIE).[1] The proprietary software of the VSC 6000 system uses measured reflectance data to compute colorimetry parameters defined by the CIE system.

The human eye has three types of cones, which receive short (blue), medium (green), or long (red) wavelengths of light. Humans perceive color because these cones are stimulated by light energy. The colorimetry parameters are called the tristimulus values, X, Y, and Z. These correspond to the human visual responses to blue, green, and red components of light. A simple calculation transforms the tristimulus into the 1976 CIE chromaticity coordinates, u',v' (Berns, 2000).

The chromaticity coordinates are a measure of visible color. If the chromaticity values for two different objects are close together, using a simple distance metric, the colors of the two objects will appear either very close or identical to the eye.

The study of the 1919–1920 postage-due stamps of Slovenia by Herendeen et al. (2011) has demonstrated the utility of the VSC 6000 not only for the measurement of color of stamps but also for actual color identification through the use of chromaticity plots. Others have also used the VSC 6000 to study color varieties of stamps themselves (DeBlois and Harris, 2011).

THE SZEGED OVERPRINTS

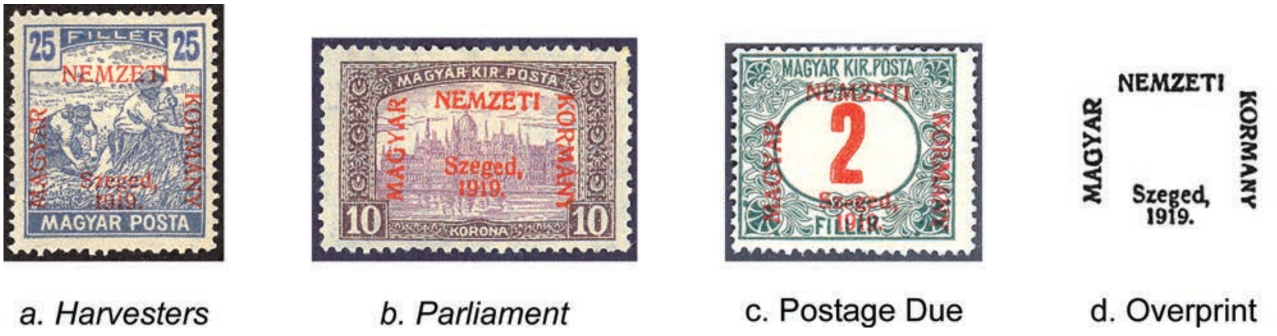
In the spring of 1919, Admiral Miklós Horthy organized a counterrevolutionary nationalist government at Szeged, a city in southeastern Hungary. This was in opposition to Béla Kun's Communist government that was in control in Budapest. As is often the case during wartime conditions, the available stamp supplies were confiscated by the group in power. The available stamps in the Szeged post office were overprinted "MAGYAR NEMZETI KORMÁNYI, Szeged, 1919" (Hungarian National Government). A total of 49 different stamps were issued (Scott numbers 1–35, B1-4, E1, J1-8, and P1) (Scott, 1998).[2] The stamps were all issued on 28 June 1919.

The stamps overprinted for use in Szeged are referenced by their design or their postal use. While there were seven of these, only the three actually used are shown in Figure 1. They are called Harvesters (Figure 1a), Parliament (Figure 1b), and postage-due stamps (Figure 1c).

The format of the overprint, used for all of the stamps, is shown in Figure 1d. Although these stamps are listed in most catalogues with the so-called Occupation issues, that is, those stamps created by occupying military forces, they were issued by a valid Hungarian authority (Ettre, 1972a:5–6; Miles, 1993:193–196). After the Horthy regime became the de facto government of Hungary, these stamps were recognized as legitimate issues of the Hungarian government (Ettre, 1972a:5–6).

The Print Shops

The production of the Szeged overprints was carried out by two different print shops (Ettre, 1972a; Brainard, 2006). Unfortunately, details of these shops have been lost to time. Since the colors of the Hungarian flag are red, white, and green, the nationalist government in Szeged decided to use red and green as the colors of the overprints. The majority of the stamps received red overprints, but stamps on which a red overprint would not show well received green overprints. The green overprint has been extensively analyzed by the author in an earlier paper (Caswell, 2012).



a. Harvesters b. Parliament c. Postage Due d. Overprint

FIGURE 1. (a, b, and c) The basic stamps used for Szeged overprints and (d) the overprint setting.

FIGURE 2. The difference in colors between (left) Print Shop 1 and (right) Print Shop 2.

As seen in Figure 2, the red overprints from the two print shops are visibly different: vermilion from Print Shop 1 and carmine from Print Shop 2. There is no visual difference between the green overprints of the two print shops. Print Shop 1 overprints of both colors can be distinguished from other overprints by the force of their application, which resulted in ink splash, that is, thickening of the ink at the edge of each letter, on the front of the stamp, and reverse embossing on the back. Print Shop 2 overprints have no distinctive features other than color.

About half of the stamps received overprints in each print shop. As will be seen, this study developed a method for attributing stamps to the two print shops.

COUNTERFEITS

Like all of the "Occupation" overprints, those of Szeged have been extensively counterfeited. The notorious Budapest stamp dealer and counterfeiter Géza Tarján produced excellent counterfeits late in 1919, apparently using the original plates (Fälschungen, 1936). Additional counterfeits originated from Prague in 1926 (Die Fälschungenplage, 1926), and there may well be counterfeits from other sources (Tyler, 1991).

For interested readers, Brainard (2006) has provided descriptions of a number of the counterfeits. Many of the counterfeits are easily recognized by bad fonts, characters, and colors. A simple example is shown in Figure 3.

Part of the research documented herein presents methods for determining how the more subtle counterfeits may be identified by precise measurements or colorimetry.

SELECTION OF TESTING SAMPLES

A preliminary examination of all of the available Szeged stamps was made in order to determine which ones were suitable for reflectance spectral measurement. Stamps with overprints that showed ink splash and embossing on the reverse were assumed to have genuine Print Shop 1 overprints. All overprints with a shifted date were assumed to be counterfeit (Caswell, 2012:37).

It was observed that in order to perform any spectrographic analyses on the overprints, a portion of the overprint must be over an unprinted portion of the stamp and the spot size must be small enough that only that portion is illuminated. If this is not the case, there may be interference by the reflectance of the underlying ink.

Most of the basic stamps with the Harvesters and the Parliament designs and the postage-due stamps have significant unprinted areas beneath parts of the overprints. Thus, with the exception of the problem described next, all of these stamps were included as samples for testing.

Under a ×10 hand lens, some candidate sample stamps were discovered to have tiny, uninked spots within the letters of the overprint. Such overprints were eliminated as samples.

a. Genuine Overprint b. Counterfeit Overprint

FIGURE 3. The poorly executed forgery on the right has a wildly different ink color than the genuine stamp on the left.

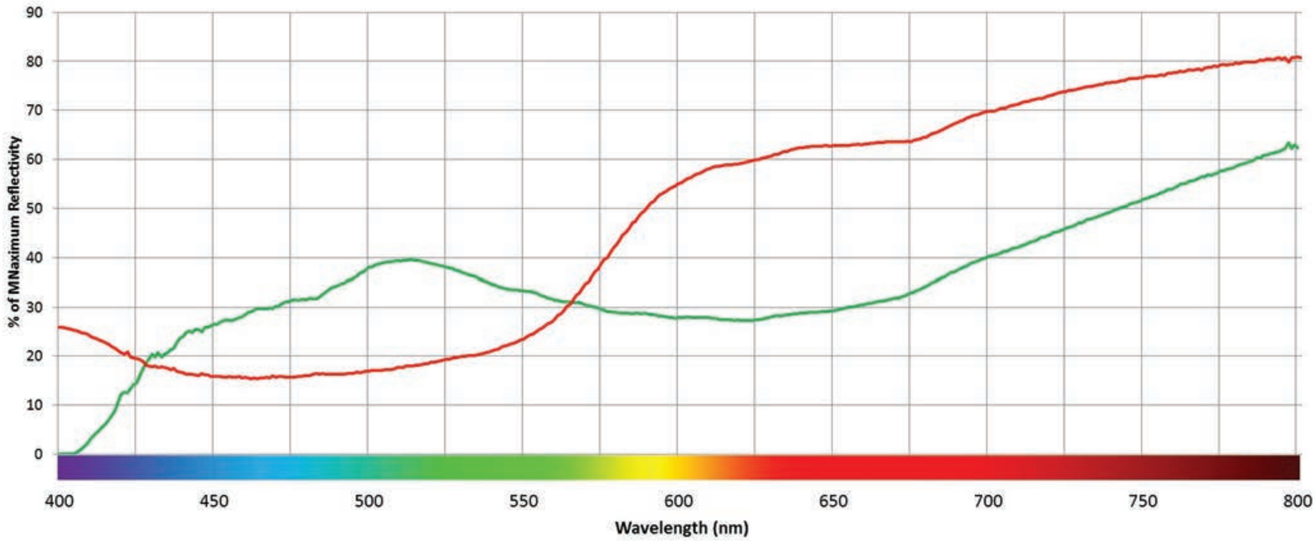


FIGURE 4. Reflectance curves from the VSC 6000 for typical red and green overprints.

TEST PROCEDURES

Each of the selected test samples was analyzed using the VSC 6000. During testing each stamp was illuminated with a 100-watt filtered incandescent spotlight. For precise measurements, the stamps were magnified by a factor of four. VSC tools for measuring and labeling the stamps were then used.

For colorimetry analysis, the reflected light was measured under ×18 magnification from a small portion of the stamp overprint having an area of 0.03 mm^2. The VSC measures reflectance as the percent of the light reflected by the sample compared to the light reflected from a standard white magnesium carbonate tile. The reflectance spectrum of each overprint was measured at a minimum of two points. The measurements were usually by different operators. The resulting spectra were averaged for each stamp. Figure 4 shows typical reflectance spectra for stamps with red and green overprints. The color of the curves in the figure matches the overprint color. The plot shows data for the wavelength range of human vision, 400–800 nanometers (nm).

RESULTS

This section presents the results of the precise measurements and colorimetric analysis of the overprints of the selected samples.

Precise Measurement

Dimensions of stamps and overprints can be measured accurately with the VSC 6000. This capability was used to measure the dimensions of the overprints of all stamps in this investigation under ×4.02 magnification. Table 1 gives a summary of the overprint measurements of the sample stamps.

TABLE 1. Precise overprint measurements of overprints by stamp design.

Stamp design	Mean horizontal distance (mm)	Standard deviation	Mean vertical distance (mm)	Standard deviation
Harvesters	14.28	±0.19	9.31	±0.19
Parliament, genuine overprint	15.67	±0.21	4.86	±0.12
Parliament, counterfeit overprint	14.29	±0.11	9.29	±0.09
Postage due, genuine overprint	16.05	±0.06	9.66	±0.03
Postage due, counterfeit overprint	14.72	±0.14	9.71	±0.06

FIGURE 5. Location of horizontal and vertical overprint measurements.

The table gives two measurements for the different stamp designs and the standard deviations of the measurements of different stamps with the same characteristics. The first are the mean horizontal distances from the foot of the "Y" of MAGYAR to the foot of the "R" of KORMÁNY (A in Figure 5). The second is the vertical distances from the foot of the first "E" of NEMZETI to the top of the "S" of Szeged (B in Figure 5).

Several conclusions may be drawn from these data:

- The measurements for the Harvesters design cannot be differentiated by overprint measurement of the sample stamps.
- The vertical distance of the counterfeit overprints on Parliament design stamps is almost double the distance of the genuine Parliament overprints.
- Comparison of the Parliament overprints with the Harvesters overprints leads to the conclusion the Harvesters setting for the overprint was used in counterfeiting the Parliament overprints.
- The horizontal distance of counterfeit overprints on the postage dues is significantly smaller than the genuine overprints. The settings the counterfeiter used were not a good match with the correct distances.

COLORIMETRIC ANALYSIS

Preliminary measurements with the VSC 6000 showed that reflectance spectra from parts of an overprint that overlay a printed portion of a stamp were ambiguous. Apparently, reflectance from the ink of the underlying design combined with the reflectance of the ink of the overprint, resulting in subtractive mixing. Useful spectra were obtainable only from parts of an overprint that lay on an unprinted part of the stamp. Thus, measurement was limited to overprinted stamps with significant unprinted areas, namely, the Harvesters, the Parliaments, and the postage-due stamps. Collecting data from overprints on other stamps would have been very difficult.

Colorimetric analyses were performed for all of the red overprint samples. Their reflectance spectra were then analyzed to determine whether CIE color models could be useful in identifying stamps from the two print shops and in differentiating between genuine and counterfeit overprints. This was not the case with the green overprints (Caswell, 2012), where the color match was so close that it is highly probable that the same ink was used.

As noted previously, it is possible to use chromaticity plots (u', v') to group samples into families of perceived colors. It has been demonstrated (Herendeen et al., 2011:108) that each group can then be enclosed in a convex hull to make the different colors easier to visualize. For the purposes of this paper, this hull is used to clearly differentiate between the three shades of the overprint.

Figure 6 presents the chromaticity plot for the carmine, vermilion, and rose-carmine overprints. It also shows the convex hulls that enclose the group of samples that have each of these colors. The carmine convex hull contains the points for both genuine Print Shop 2 overprints and counterfeit overprints. The convex hull for the vermilion overprints contains genuine Print Shop 1 overprints. The lack of overlap of these convex hulls is in agreement with the observation that the colors of these overprints are visually different. The unusually shaped rose-carmine convex hull is disjoint from the other two, which is consistent with its different color. Szeged overprints of the rose-carmine color have not previously been described in the philatelic literature.

Figure 7 compares the convex hull of genuine Print Shop 1 overprints (Hull A) with the convex hulls of other varieties. The convex hull of the carmine overprints, shown in Figure 6,

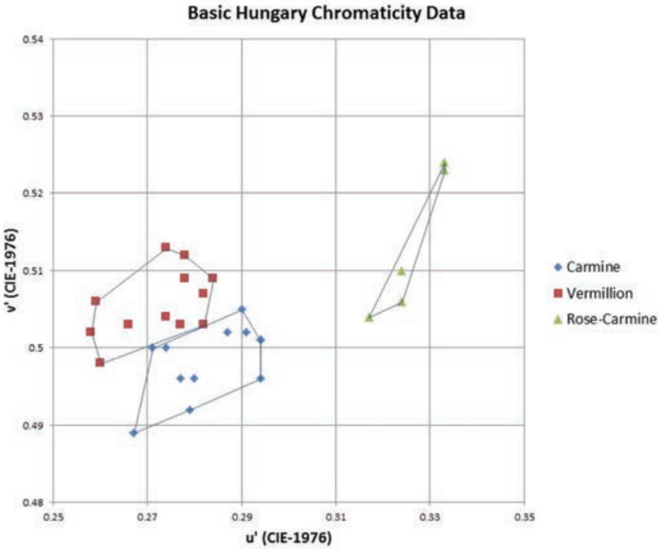


FIGURE 6. Convex hulls for the red-colored overprints.

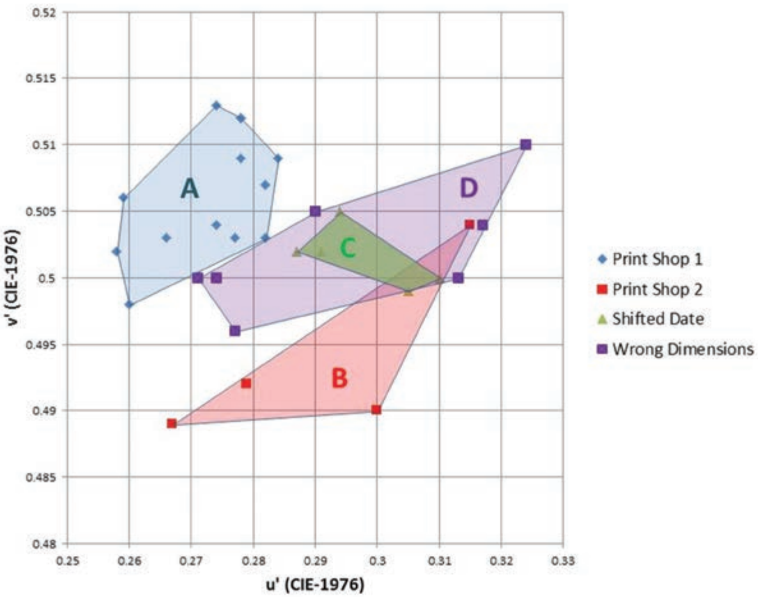


FIGURE 7. Identifying print shops by carmine colors.

is partitioned into three convex hulls, showing the distribution of points for

- genuine Print Shop 2 overprints (Hull B),
- shifted date overprints (Hull C), and
- wrong dimension overprints (Hull D).

The small overlap of Print Shop 2, shifted date, and wrong dimension overprints is due to the similarity in color of these overprints. The Print Shop 2 overprints are significantly distant from the Print Shop 1 overprints, again indicating a clear difference in color. The observation that the convex hull of the wrong dimension overprints (Hull D) lies outside the convex hull of genuine Print Shop 1 overprints (Hull A) and has only slight overlap with the hull of Print Shop 2 (Hull B) is in agreement with Brainard's new conclusion that the wrong dimension overprints are counterfeit,[3] rather than a genuine variety, as stated by Ettre (1972a). The convex hull of the shifted date overprints lies within the convex hull of the wrong dimension overprints because these overprints are the same color. They are therefore two varieties of counterfeits in agreement with the literature, Brainard states.

CONCLUSIONS

This study has demonstrated a useful methodology for analysis of colored overprints. The VSC 6000, through use of its capabilities to make precise measurements of stamps and to perform colorimetric analyses, has been shown to be a powerful tool for studying overprints.

The finding that the convex hulls for the overprints with the wrong dimensions lie outside of the convex hulls for genuine overprints was very important. It showed there was a significant color difference, thus confirming Brainard's (2011) conclusion that the wrong dimension overprints are counterfeit.[4] This corrected an earlier assumption (Ettre, 1972b) that they are genuine varieties. Both wrong dimension overprints and shifted date overprints fail to match the convex hull color characteristics of either the Print Shop A or Print Shop B overprints. These data are in agreement with Brainard's conclusions that they are two varieties of counterfeits.

ACKNOWLEDGMENTS

This work was supported in part by a grant from the Institute for Analytical Philately, Inc. (IAP). I thank David L. Herendeen, president of IAP, for his encouragement and support and for providing the software for computing convex hulls. Thanks are also due to Thomas Lera, Winton M. Blount Chair in Research at the Smithsonian National Postal Museum. Not only did the NPM provide the VSC 6000, but Mr. Lera also assisted in training the author in the use of the device and in data collection. Finally, thanks to Christopher E. Brainard, who provided a transcript of his notes on his study of the Szeged overprint proofs.

NOTES

1. CIE, the Commission Internationale de l'Éclairage (International Commission on Illumination), formed in 1913, is the international organization that develops standards for everything having to do with light and color. They have had a number of color standards through the decades used for color matching. For more information, visit their Web site at http://www.cie.co.at/main/ (accessed 6 September 2012).

2. Scott numbers (Scott Publishing Co., 1988) are given for reference, but specialized European catalogues may list more varieties.

3. C. E. Brainard, email message to author, 31 May 2011.

4. Brainard, email message.

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A Comparative Study of Security Measures Used by Stamp Printers

Garfield Portch and Charles J. G. Verge

The purpose of this paper is to document the learning steps undertaken by the authors to understand the features of the Foster + Freeman, Ltd. Visual Spectral Comparator (VSC 6000) for use in expertizing philatelic submissions at the Vincent Graves Greene Philatelic Research Foundation. With no published guide to the philatelic use of this machine to render expert opinions, there was a need to discover its applications and processes. As a project, the authors undertook to look for, discover, identify, and compare the individual and common security features used by Royal Mail in the United Kingdom and by the Canada Post Corporation in Canada during the production of their high-value definitives in the 1980s, 1990s, and 2000s, including Canada's $10 Blue Whale definitive—2010 (Figure 1). After familiarization with some of the VSC 6000's many features, the authors applied their newfound skills to a tobacco excise stamp recently introduced in Canada before using philatelic material sent in by clients to the Greene Foundation's expert committee. Each of the steps of the project is detailed in this paper. The complete paper will be published in *The Canadian Philatelist* and the PowerPoint presentation can be found at http://www.analyticalphilately.org/symposium.html.

FIGURE 1. Canada's highest-value denomination and largest stamp: the $10 Blue Whale. The use of fluorescent inks for the scuba diver and the krill is shown using ultraviolet light at 365 nm. Courtesy the Greene Foundation.

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Abstract received 10 April 2013; accepted 26 April 2013.

New Ways of Looking at Prephilatelic Inks

Dieter Bortfeldt

This PowerPoint presentation describes investigations carried out over the last two years studying the authenticity of inks used for postal markings on colonial stampless letters (Figure 1). After exploring various possibilities, a new spectrophotometric method, called CONTRA TEST, has been developed. The presentation presents the details of this method and shows it is a viable way to expertize such preadhesive items. When spectral curves intersect at three or more points, the color obtained presents differences in composition, which in turn suggests that the color is difficult to reproduce. One would need to know the nature of the pigments and color measuring systems in order to forge the color and composition of the ink. The PowerPoint presentation can be found at http://www.analyticalphilately.org/symposium.html.

FIGURE 1. Colonial letter from Santiago, Chile, to Lima, Peru. Courtesy of the Ponce Collection, Lima, Peru.

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A Layman’s Forensic Adventure

Roland H. Cipolla II

This PowerPoint presentation describes how current developments in analytical philately were used by a layman, that is, someone without formal scientific training, to determine that an exciting, newly discovered U.S. postal history item was not a fake. Access to the equipment used was provided by the Smithsonian National Postal Museum. It included the Foster + Freeman, Ltd. Video Spectral Comparator 6000, the Bruker Tracer III SD X-Ray Florescence Analyzer, and the Bruker Alpha FT-IR. The author used these analytical tools to determine if there were any anomalies along the cut sides of a bisected stamp, the application of the cancellation, or the chemistry of the sheet to which the stamp was applied (Figure 1). The PowerPoint presentation can be found at http://www.analyticalphilately.org/symposium.html. A detailed article was published in *The Chronicle* (Cipolla, 2013) and in the 26 March 2013 Robert A. Siegel Auction Catalog, Sale 1041A.

FIGURE 1. Diagonal half of a 1¢ 1851 U.S. stamp, type 4, tied by a “NEW HAVEN CONN JUL 29” circular date stamp to a printed circular, internally dated 1853 and addressed to Hartford. Image courtesy of the author.

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Scholarships at the Smithsonian National Postal Museum

The Smithsonian National Postal Museum (NPM) is pleased to announce five scholarships, available to scientific, academic, and philatelic scholars, for the research of postal operations, postal history, and postage stamps, including scientific analysis. The purpose of the scholarships is to enable a block of uninterrupted project research time in the NPM or other Washington, D.C., libraries and access to its scientific equipment to help solve philatelic questions. Research can include any topic supported by the NPM collections, including the international collections, research in the history of the post in any century, or scientific analysis of personal collections. The end result of the research will be publication as a dissertation, an original article, or a chapter in a book.

Scholarships are from the Smithsonian National Postal Museum and the Confederate Stamp Alliance (CSA), the United States Stamp Society (USSS), 2006 World Philatelic Exhibition, and National Philatelic Exhibitions of Washington, D.C., Inc. (NAPEX).

Applications will be accepted throughout the year for these scholarships, which range from $500 to $2,000.

Applications should include

- an outline of the subject to be studied and how it relates to the applicant's previous philatelic, scientific, or postal operations or postal history research;
- intentions as to publication of the results after completion of the project;
- an accurate cost of the trip(s), including places and organizations to be visited and collections to researched; and
- a short curriculum vitae (including personal details, collecting interests, previous publications, and philatelic achievements).

For additional information and application for each scholarship, see http://www.postalmuseum.si.edu/scholarships/index.html or e-mail npmresearchchair@si.edu.

Application for an IAP Research Grant

The initial application should include information describing yourself and your proposed research effort. This information will be used to evaluate the merits of the proposed work and its relationship to the mission of the Institute for Analytical Philately, Inc. (IAP). You will then be contacted by one of the institute's directors to further discuss your proposal. The greatest weight is given to projects that develop new methodologies promising to be of lasting significance to philately.

Good proposals result from clearly thought-out plans for your project. The organization of a proposal should always be the same because you are trying to convince a "buyer" that you are "selling" a great product. The proposal should include the following information.

EXECUTIVE SUMMARY

This section should describe the project you plan to do, why it important, and how it will benefit philately. This is where you get to shine. Write this section for a manager who has no idea of what the technical details are but who can immediately grasp the potential and importance of your idea.

TECHNICAL APPROACH

This is the technical meat of your proposal. In this section, describe the tasks you will perform and the manner in which you plan to perform them successfully. Ideally, you should also estimate the scope (for our purpose in elapsed calendar time) so you will later be able to develop a project schedule.

STATEMENT OF WORK

This is a recap of the tasks you have defined in the Technical Approach and can be used to determine if your plan is succeeding. It is also incorporated in the Research Grant

Agreement you enter into with IAP. In many cases, the Technical Approach and Statement of Work can be combined.

COST AND SCHEDULE

Estimate the amount of funding you will need to perform your effort, remembering that all IAP grants are *firm, fixed-price agreements*, and agreeing to perform the tasks set forth in the Statement of Work for a set fee. Grants typically range from $2,000 to $4,000 and are intended to help fund travel, lodging, and laboratory use. Additional funding may be available through cost sharing with alliance members, who can also provide advice on previous work done in a particular area or help in conceiving and planning a research effort. (See the Preface on page vii.)

FINAL REPORT AND PUBLICATION

In this section you present an outline of how you expect your final report will look and indicate the technical and philatelic journals to which you will submit your article or paper beyond possible publication under IAP auspices.

RÉSUMÉ

In this section you provide a summary of both your professional and philatelic accomplishments. It is neither necessary nor desired that you provide long lists of technical papers you may have authored during your career. It sufficient to make statements such as ". . . resulting in dozens of journal articles." A professional scientific background simply adds additional credence to your proposal and helps convince the reviewer there is a good probability the project will satisfy its goals.

Additional information and application for each research grant can be found at http://www.analyticalphilately.org/applyingforagrant.html.

The Symposium Feedback Session

EQUIPMENT

Suggestion: Provide a summary of machine abilities to allow both IAP directors as well as applicants to determine likelihood of research problem success (in simple English).

Answer: We plan to do this.

Question: Is it possible to develop a method to measure the age of gum? Some early stamps were used without any cancellations, so one could forge a cover where cancellations were not used.

Answer: Many gums were used, more than most people think, especially for the classic stamps. Moreover, gum and gum recipes are very complex compounds (natural products) of the basic elements carbon, hydrogen, and oxygen. So analytical “fingerprints” are not as clear or certain. However, if modern antioxidants are detected, say, by Fourier transform infrared (FTIR) or wet analyses (like butylated hydroxytoluene (BHT) or the like), then the gum is a modern gum. Classic gums did not incorporate antioxidants for quality purposes. Not all modern gums possess them, either. So if they are not detected, then the gum can be modern or earlier. This is not likely and not easily done no matter the expense allowed.

Question: Has the Video Spectral Comparator 6000 (VSC 6000) been used on hand-stamped overprints?

Answer: Yes, but there are limitations.

Question: When using proton-induced X-ray emission (PIXE), what irradiation time starts leading to sample damage?

Answer: Usually greater than 5 minutes.

Question: Can X-ray fluorescence spectrometry (XRF) be used to determine differences in sizing or coating for heavier elements?

Answer: It depends and is on a case-by-case basis.

Question: When using PIXE, how long is the sampling time compared with XRF?

Answer: About the same.

Comment: Be careful when interpreting what the presence of a cation means. Without identifying the compound, one cannot be sure whether the origin was sizing, brightener, filler, etc.

Question: Is the VSC 6000 easy to use for the average collector?

Answer: Yes—very easy to learn!

Question: Can we ask manufacturers to provide basic performance characteristics of their instruments, especially the VSC 6000, or should we document and distribute them, for example: beam size, detection units, precision of measurements, interferences, calibration, linear range, etc.?

Answer: This is available in the handouts and Wednesday is hands on with the manufacturer representatives.

Question: Can elemental analyses be used to evaluate cancels?

Answer: Yes.

Question: To determine relative proportions of elements in an XRF-tested sample, can one simply integrate the area under the curve?

Answer: Sometimes this can be done when the atomic numbers of the elements are close together. Otherwise, go to the National Institute of Standards and Technology (NIST) Web site (www.nist.gov) for absorption data.

COLOR

Question: Are shades due to the inks or the paper (aging, environmental effects, etc.)?

Answer: Both.

Question: Can we define spectrographically what determines shade differences?

Answer: Sometimes.

Question: Using White's color plates as a basis, can we define the spectra of classic U.S. stamps?

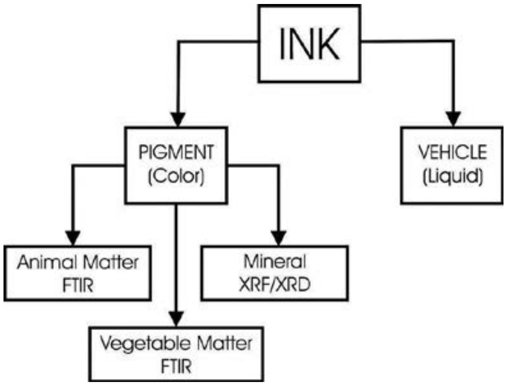
Answer: Not likely. White's color plates are pretty accurate for the narrow group of stamps they refer to, but beyond that, they are very limited in applicability given the great range of colors that exist in philately.

Suggestion: We need to document the effects of various treatments on color, for example, washing, UV exposure, fingerprints, etc.

Answer: Absolutely; we are looking for the researcher.

Question: What is a dye? What is a pigment?

Answer: Inks are composed of pigments (the color) and vehicles (the liquid) (Figure 1). As shown below, pigments may be animal matter, vegetable matter, or minerals. Each type of pigment can be identified by the noted analytical device (also note that dyes are often deposited on minerals).



Question: Are there color portfolios that can be used to verify color varieties?

Answer: Some exist, like Ridgway, Pantone, Munsell, etc., but they are not adequate.

PAPER

Question: Permeability: Does ink deposit change it, and does permeability change over the surface of the stamp?

Answer: Yes to both.

Question: I have heard the word glaze applied to paper. How does this differ from sizing?

Answer: In general, at the most elementary level, most sizing is added at the wet end and a glaze is added to finished paper. However, there is surface sizing as such which often uses some of the same chemicals/coatings that might create a "glaze." What is referred to in Scott's as glazed paper is a little of a stretch so far as glazes go. It was definitely heavily calendared but with no obvious coating like most modern glazed papers would have. So it is all not quite so black and white. It is not clear if paper in question could be analyzed for a "finished coating/glaze that was added during finishing."

Question: Is it possible that the Continental Bank Note Co. paper is denser than that of National?

Answer: Yes, by 3.5% (due to fines?).

Question: In the upper-right modulus graph (J. H. Barwis, Paper Characteristics of U.S. 3¢ Stamps, 1870–1881, this volume), why is R2 1/10th that of the other three?

Answer: No one knows!

INKS

Question: How did Grinnells get the inks of the genuine stamps?

Answer: This is not a correct statement. The inks had different chemical compositions. See Pearson, Patrick Chilton (2006), *The Investigation of the Grinnell Hawaiian Missionaries by the Expert Committee of the Royal Philatelic Society London*, page 67, London: The Royal Philatelic Society.

Question: How can one clear the background of a negative cancellation so it stands out and becomes readable?

Answer: This can be done with Photoshop.

STATISTICS

Question: Statistical population estimates appear to have asymmetric confidence intervals. Why?

Answer: The confidence interval is modified because we know the lower bound from the number of existing stamps. This makes the interval asymmetric.

Suggestion: At the end of the statistics lecture, include info on what to do next.

Answer: Great idea—will do.

Suggestion: How about developing a statistical model of preservation rate on cover versus how many observed and how many printed?

Answer: Good potential project idea.

EXPERTIZATION

Comment: Can we urge the various expert groups to include detailed reasons for "not genuine?"

Answer: Some do; it is becoming more common, but there is still a long way to go.

Question: Can watermarks be identified without removing a stamp from a cover?

Answer: Yes, in some cases, with the use of the VSC 6000.

Comment: On postal history items, ask the expert why he believes something to be genuine. It would encourage the expert to deal more deeply with the whole subject.

Answer: Again, most expert groups do "historical research," but they have not gotten into the habit of sharing the information.

Suggestion: How about an international board to decide which experts should be accepted to avoid auction houses shopping around for a "good" certificate on an item already decided to be bad?

Answer: There is such an organization, the Association International des Experts en Philatelie (AIEP). Check their Web site, www.aiep-experts.net.

Comment: Certificates shouldn't be older than five years due to technical developments.

Answer: That is up to the owner, purchaser, or exhibitor. We have seen environmental changes to objects, which should also mean a new certificate should be obtained.

INTO THE FUTURE

Question: Would you plan to attend a Second International Symposium (Y or N)?

Answer: Y (100%).

Question: Would you recommend attending a future symposium (Y or N)?

Answer: Y (100%).

Question: Would you personally use any of the technology presented (Y or N)?

Answer: Y (100%).

Question: Do you think others you know might use any of the technology presented (Y or N)?

Answer: Y (100%).

Question: Could you please give the three geographical locations you would prefer for a symposium (e.g., Washington, New York, London, etc.)?

Answer: While there was some support for other venues, the overwhelming vote was for the NPM because of the ability to have the hands-on workshops.

Question: How often do you think the International Symposium should be held (two, three, or four years)?

Answer: Two years (70%). This was again the overwhelming choice and probably optimum for having quality research papers.

Question: What time of year do you think the symposium should be held?

Answer: Most liked November time frame or other off-season times.

REQUIREMENTS FOR SMITHSONIAN SERIES PUBLICATION

ALL MANUSCRIPTS ARE REVIEWED FOR ADHERENCE TO THE SISP MANUSCRIPT PREPARATION AND STYLE GUIDE FOR AUTHORS (available on the "Submissions" page at www.scholarlypress.si.edu). Manuscripts not in compliance will be returned to the author. Manuscripts intended for publication in the Contributions Series are evaluated by a content review board and undergo substantive peer review. Accepted manuscripts are submitted for funding approval and scheduling to the Publications Oversight Board.

MINIMUM MANUSCRIPT LENGTH is thirty manuscript pages. If a manuscript is longer than average, an appropriate length will be determined during peer review and evaluation by the Content Review Board. Authors may be asked to edit manuscripts that are determined to be too long.

TEXT must be prepared in a recent version of Microsoft Word; use a Times font in 12 point for regular text; be double spaced; and have 1" margins. Each chapter/section must be saved in a separate file.

REQUIRED ELEMENTS are title page, abstract page, table of contents, main text, and reference section. See the SISP Manuscript Preparation and Style Guide for Authors for the order of all elements.

HEADINGS should be styled so different levels of headings are distinct from each other and so the organization of the manuscript is clear. Insert one line space above and one line space below all headings.

FRONT MATTER should include title page, abstract page, and table of contents. All other sections are optional. Abstracts must not exceed 300 words. Table of contents should include A-, B-, and C-level headings.

TABLES (numbered, with captions, stubs, rules) should be submitted in separate MS Word files; should include footnotes, if appropriate; should have rules only at top, bottom, and beneath column heads. Print outs of each table should accompany the manuscript to ensure correct layout of data. Tabulations within running text should not be numbered or formatted like formal tables, and should be included in the text of the manuscript.

FIGURE CAPTIONS should be provided in a separate MS Word file.

FIGURES (e.g., photographs, line art, maps) should be numbered sequentially (1, 2, 3, etc.) in the order called out; be placed throughout text, not at end of manuscript; have all components of composites lettered with lowercase letters and described in the caption; include a scale bar or scale description, if appropriate; include any legends in or on the figure rather than in a caption.

ART must not be embedded in the main text.

Figures must be original and submitted as individual TIFF or EPS files. Resolution for art files must be at least 300 dpi for grayscale and color images and at least 1200 dpi for line art. Electronic images should measure no more than 100% and no less than 75% of final size when published. JPG files will not be accepted. Color images significantly increase costs so should be included only if required. Funding for color art is subject to approval by SISP and the Publications Oversight Board.

TAXONOMIC KEYS in natural history papers should use the aligned-couplet form for zoology. If cross referencing is required between key and text, do not include page references within the key but number the keyed-out taxa, using the same numbers with their corresponding heads in the text.

SYNONOMY IN ZOOLOGY must use the short form (taxon, author, year:page), with full reference at the end of the paper under "References."

IN-TEXT REFERENCES should be used rather than bibliographic notes and should follow the author-date system in the following format: "(author last name, year)" or ". . . author (year)"; "(author, year:page used within the text)" or ". . . author (year:page)." A full citation should be included in a "References" section.

ENDNOTES are to be used in lieu of footnotes and should be keyed manually into a separate MS Word file, in a section titled "Notes". Notes should not contain bibliographic information. Manually type superscript numerals in text and use full-sized numerals at the beginning of each note in the "Notes" section. SISP will determine the best placement of the notes section, either at the end of each chapter or at the end of the main text.

REFERENCES should be in alphabetical order, and in chronological order for same-author entries. Each reference should be cited at least once in main text. Complete bibliographic information must be included in all citations (e.g., author/editor, title, subtitle, edition, volume, issue, pages, figures). For books, place of publication and publisher are required. For journals, use the parentheses system for volume(number):pagination [e.g., "10(2):5–9"]. Do not use "et al."; all authors/editors should be included in reference citations. In titles, capitalize first word, last word, first word after colon, and all other words except articles, conjunctions, and prepositions. Examples of the most common types of citations are provided in the SISP Manuscript Preparation and Author Style Guide.

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