

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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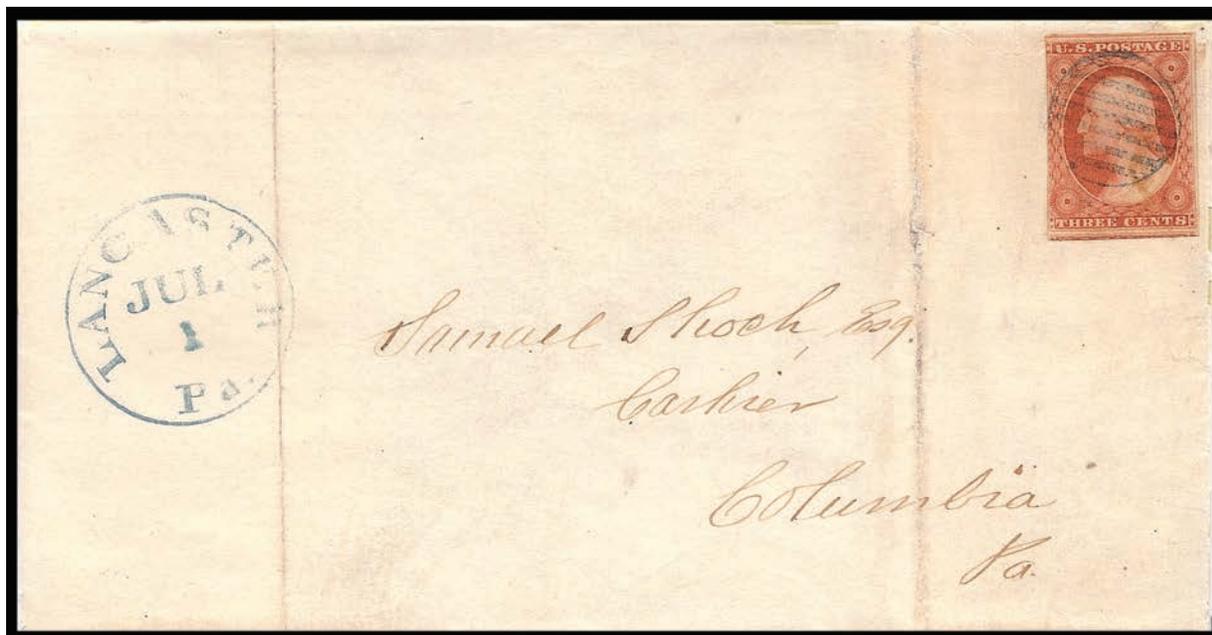


FIGURE 1. Orange-brown color (Scott 10A) first-day cover, 1 July 1851. Courtesy of the author.

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

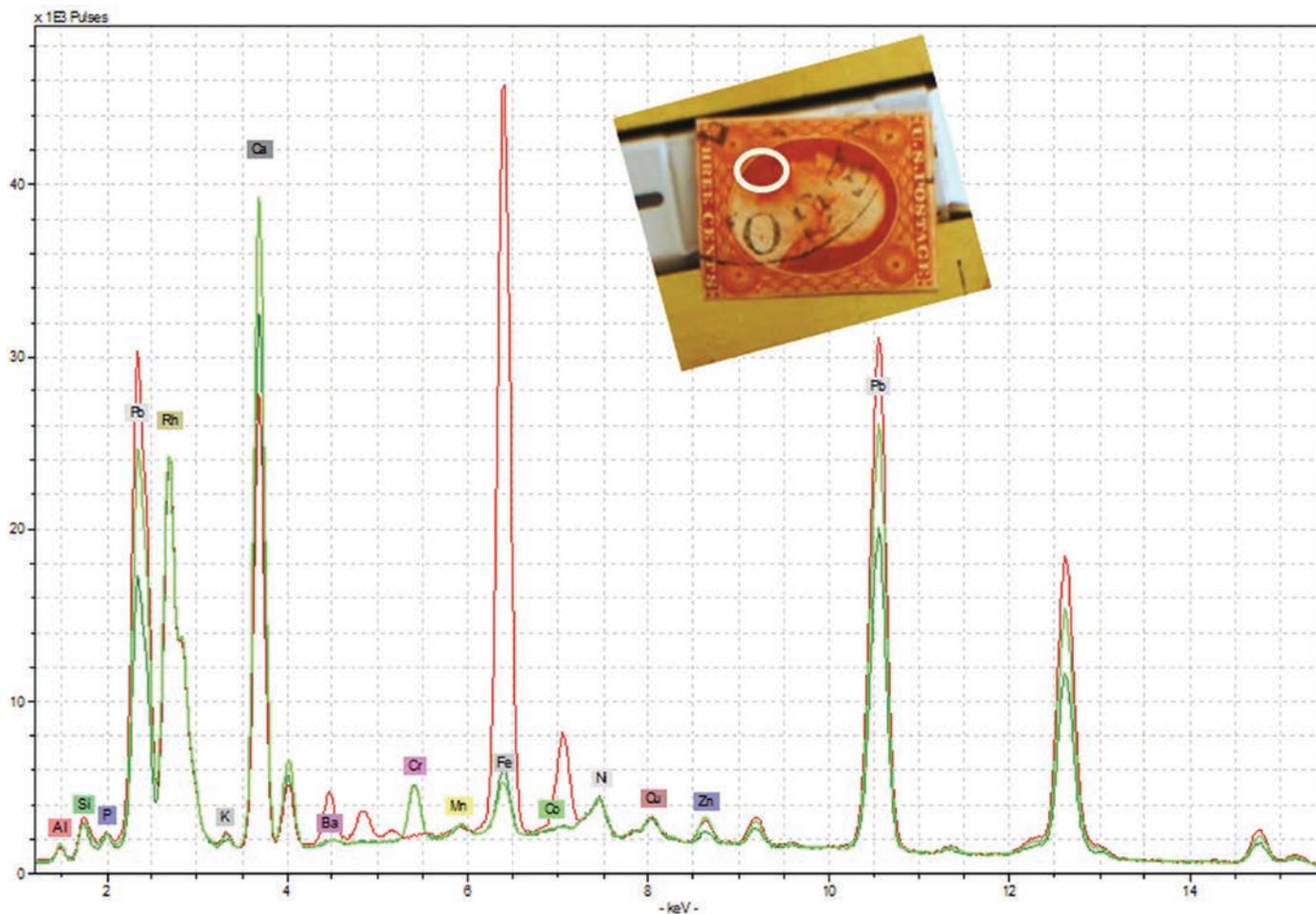


FIGURE 4. Typical X-ray fluorescence spectrograph, illustrating portion of stamp ink for three different samples of Scott 10A. The white oval on the inset stamp is the approximate sample size. Courtesy of the author.

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

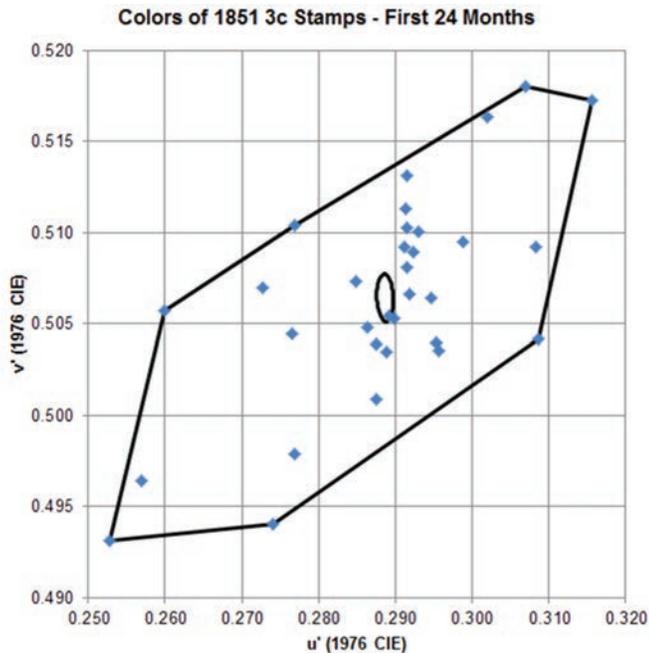


FIGURE 5. Chromaticity plot of 1851 3¢ stamps.

(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

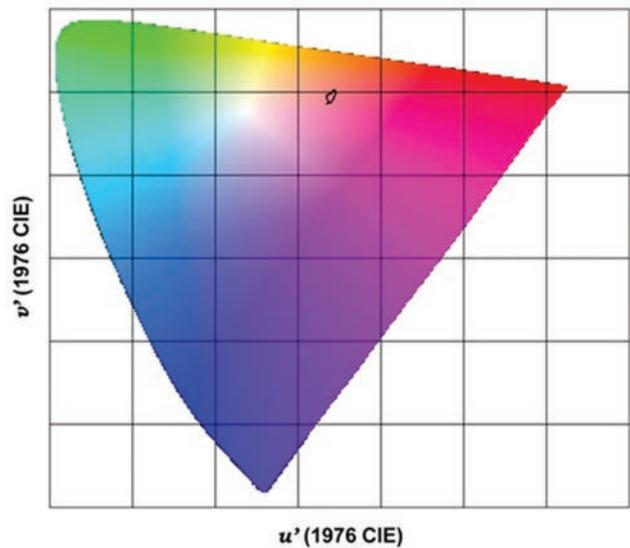


FIGURE 6. Location of 3¢ stamp colors in full 1976 CIE color gamut.

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



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

^aResults 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



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

^aResults from the L1 energy level.^bContamination 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, CaSO₄. 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 (PbCrO₄), 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

^aResults from the L1 energy level.^bContamination suspected from orange-brown pigment.^cEarliest 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).

REFERENCES

- Amonette, W. F. 1973. Color Study of the Three-Cent Stamp of the United States 1851–57 Issue. *Chronicle of the U.S. Postal Issues*, 25(2):85–91.
- Amonette, W. F., and W. Hulme. 2005. Color Study of the 3¢ Stamp of the United States 1851–1857 Issue: An Update. *Chronicle of the U.S. Postal Issues*, 57(2):103–109.
- Beals, D., III. 1974. Colors of the Three Cent 1857–61 Perforated Type II Stamps (54 and 55). *Chronicle of the U.S. Postal Issues*, 26(1):14–17.
- Billmeyer, F. W., Jr., and M. Saltzman. 1981. *Principals of Color Technology*. 2nd ed. New York: Wiley-Interscience.
- Card, D. A. 1964. Some Thought about the Colors of the 3¢ 1851 (S1 and S2) Stamp. *Chronicle of the U.S. Postal Issues*. 17(1):6–10.
- Chase, C. 1942. *The 3¢ Stamp of the United States 1851–1857 Issue, Revised*. Lawrence, Mass.: Quarterman Publications.
- Eastaugh, N., V. Walsh, T. Chaplin, and R. Siddall. 2008. *Pigment Compendium, A Dictionary and Optical Microscopy of Historical Pigments*. Amsterdam: Elsevier.
- Ellis, C. 1940. *Printing Inks, Their Chemistry, and Technology*. New York: Reinhold Publishing Corporation.
- Foster + Freeman, Ltd. 2011. *VSC 6000. Video Spectral Comparator Software Manual*. Worcestershire: Foster + Freeman.
- Granzow, G. W. 2004. The Plates of the 1851–1857 3¢ Stamps of the United States, Part III: Perforated Stamp Plates of 1857–60. *Chronicle of the U.S. Postal Issues*. 56(4):263–268.
- Herendeen, D. L., J. A. Allen, and T. Lera. 2011. Philatelic Shade Discrimination Based on Measured Colour. *London Philatelist*, 120:105–117.
- Higgitt, C., M. Spring, and D. Saunders. 2005. Pigment-Medium Interactions in Oil Paint Films Containing Lead-Based Pigment. *WAAC Newsletter*, 27(2): 12–16.
- MacAdam, D. 1942. Visual Sensitivities to Color Differences in Daylight. *Journal of the Optical Society of America*, 5:247–274. <http://dx.doi.org/10.1364/JOSA.32.000247>.
- Sayers, G. 2009. Production Plate Varieties and the Nature of Opaque Inks, with Notes on the Post Office “Scummy” Printings. *Chronicle of the U.S. Postal Issues*, 61(4):310–325.
- Scott Publishing Co. 2012. *2012 Specialized Catalogue of United States Stamps*. Sidney, Ohio: Scott Publishing.
- Toppan, Carpenter, Casilear, & Co. 1851. Correspondence, #169, June 10, 1851, as Transcribed by Wilson Hulme. Washington, D.C.: Smithsonian National Postal Museum.
- Wyszecki, G., and W. S. Stiles. 2000. *Color Science*. New York: Wiley-Interscience.