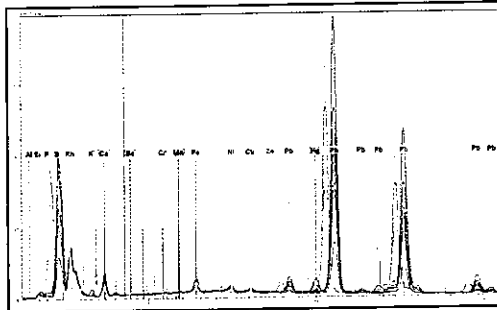
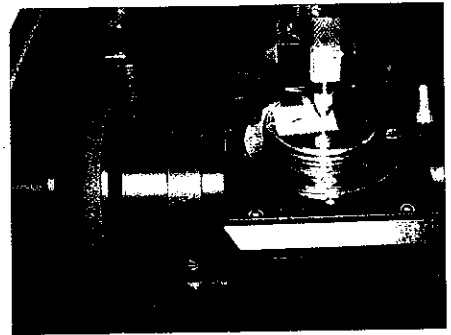


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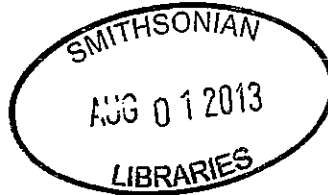
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of the U.S. Classic Postal Issues



In our 1847 section, Wade E. Saadi uses X-Ray fluorescence analysis to show that the pigment in the 5¢ 1847 stamps, despite the wide variety of shades and printings, was almost based on lead, rather than iron oxide.

In our 1861 section, Harry G. Brittain uses infrared absorption spectroscopy (among other techniques) to analyze the chemical composition of the ink and paper of the 1¢ 1861 stamps.



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FORENSIC ANALYSIS:
COMPOSITION OF INK AND PAPER OF THE 1¢ 1861 STAMP

HARRY G. BRITAIN, PhD, FRSC

The onset of the Civil War caused the Federal government to demonetize all supplies of the existing 1851 and 1857 stamps, and to issue a set of newly designed stamps to be used in the Union States. The Post Office Department awarded a printing contract to the National Bank Note Company of New York, and the new stamps began to appear in August, 1861. The earliest documented off-cover use of the 1¢ Franklin stamp (Scott 63) is August

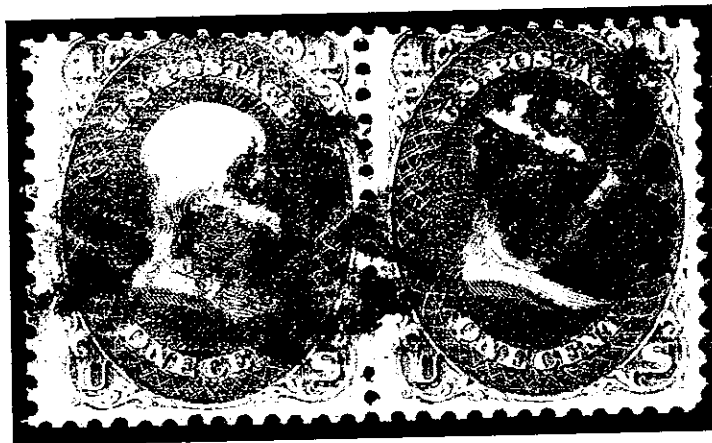


Figure 1. Scott 63 pair, from the author's collection. The region sampled for ink analysis was from the blue area just below the vignette on the right stamp, and the region sampled for paper analysis was the uncanceled area between the stamps.

17, 1861, and the earliest on-cover use is August 21. Approximately 150,000,000 1¢ stamps were printed using five plates (numbers 9, 10, 22, 25, and 27). The colors of these stamps ranged from pale blue through dark blue.¹ Figure 1 shows a pair of the 1¢ Franklin stamp.

The central design of the stamp was taken from a bust executed by Jean Antoine Houdon. These stamps were used to prepay the drop letter rates for local delivery, the rates for circulars and newspapers, the fee for carrier service (prior to July 1, 1863), book rates, and various third-class rates.

In order to evaluate the composition of inks used to print the 1¢ Franklin stamps of the 1861 series, infrared absorption spectroscopy (coupled with attenuated total reflectance sampling) was used to study the stamp surfaces.² Through comparison with appropriate

reference standards, the components of the printing ink were identified. In addition, the existence of an interesting product formed by the interaction of a pigment component and dispersing oil was detected.

Primer on infrared absorption spectroscopy

The patterns of intramolecular motion existing in molecules are characterized by repetitive oscillations of atoms about the center of gravity of the molecule, and these correlated motions are termed the vibrational modes of the molecule. The energies required to cause molecules to enter into higher states of molecular motion lie within the range of 400 to 4000 wavenumbers, falling into a region of the electromagnetic spectrum known as the mid-infrared 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.³ For many 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, and as a result the technique is referred to as FTIR spectroscopy.

The principles underlying the absorption of infrared energy by molecules can be understood by considering that since every molecule possesses only a finite number of molecular vibrational modes, a molecule can only absorb 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 total of these infrared absorptions is termed its absorption spectrum.

While the energy associated with a particular molecular vibrational mode is readily identified from the literature,⁴ 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. In typical practice, the FTIR spectra of appropriate reference materials are obtained, and these are compared to the spectrum of the unknown sample. When an 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 obtaining FTIR spectra of stamp surfaces is that of attenuated total reflectance (ATR). To use ATR sampling, one simply clamps the stamp onto the surface of an analyzing crystal to ensure a sufficient degree of optical contact. Infrared radiation is passed through the crystal at an angle that causes the light to undergo total internal reflection, and at each reflection the radiation penetrates a small distance beyond the crystal into the sample. One obtains the FTIR spectrum from analysis of the modification of the incident infrared beam caused by absorbance of the stamp. Because the internal reflectance process does not permit the infrared beam to pass very deeply into the sample, the ATR sampling method enables one to effectively study only the inked layer of a stamp.

In this study, Fourier Transform infrared absorption spectra were obtained at a resolution of 4 wavenumbers (i.e., 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, where the samples were clamped against the zinc selenide (ZnSe) crystal of a Pike MIRacle single reflection horizontal ATR sampling accessory. This particular ATR sampling device enables one to study an approximate one square millimeter area of a stamp. The use of the device for forensic stamp analysis is illustrated in Figure 2. In the illustration, the stamp has actually been mounted upside down in order to demonstrate the small spot size (under the tip of the pressure clamp) studied in each measurement.

Studies of the 1¢ 1861 stamp surfaces

While the exact details of ink compositions, and methods for their manufacture, that were used to print postage stamps of the 19th century are not absolutely known, a sufficient body of knowledge does exist and a general discussion of the inks used in intaglio printing is available.⁵ Sayers has recently written that mineral pigments were used almost exclusively at this time, and were mixed with at least a drying oil (typically linseed oil), a surfactant (typically a soft soap), and a solvent.⁶ This mixture was homogenized through the use of a ball-milling process to produce a colloidal dispersion of ink pigments in the vehicle. Granzow has described the process used by Perkins Bacon to produce print "oil," where the formulators first heated linseed oil and beeswax until slightly burned; then they added soft soap to disperse the pigment, and finally turpentine to thin the oil to a desired viscosity.⁷ While most of the turpentine would volatilize during the drying process, the other oil components would remain in the dried ink layer on the surface of the stamp.

Figure 3 contains the FTIR spectrum of the blue ink portion of the Figure 1 pair, along with the FTIR spectrum obtained from the unprinted paper area. It is evident in this illustration that the ink used to print the Scott 63 stamps contains several absorption bands not present in the FTIR spectrum of the paper. The origin of the peaks observed at an energy of approximately 2090 wavenumbers (arrows in Figure 3), which are due to the symmetric stretching mode of a cyano -CN group, are extremely easy to identify as being due to the presence of the blue pigment Prussian blue. This compound has a chemical formula which can be written as $\text{FeK}[\text{Fe}(\text{CN})_6]$, and is known to exhibit an intense blue color.

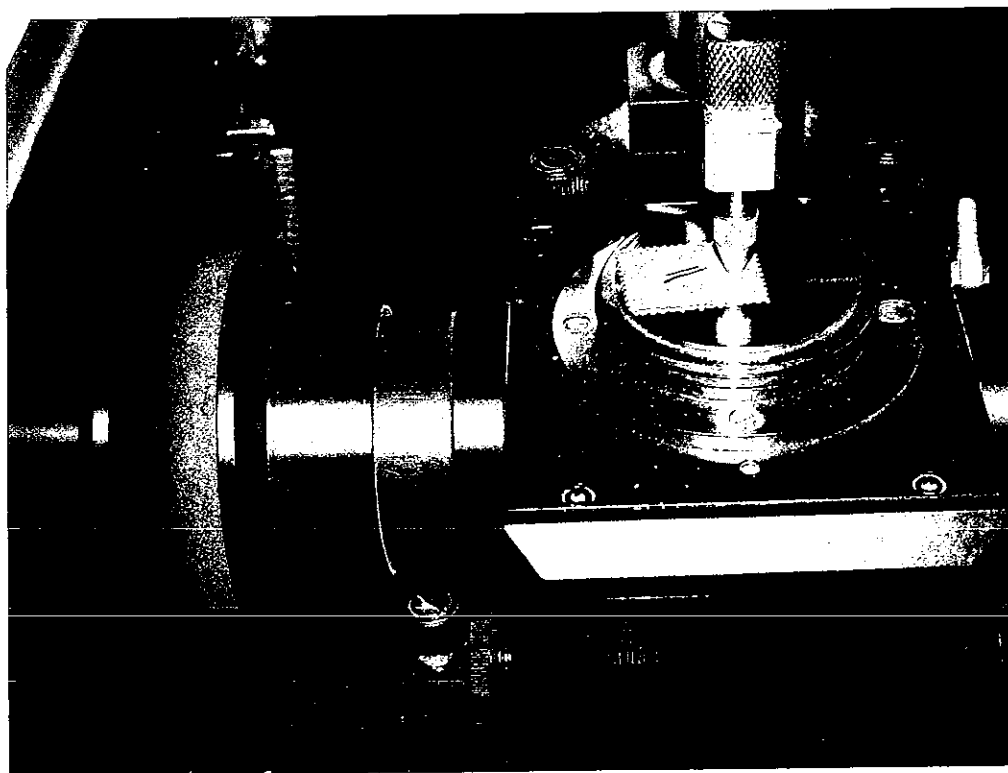


Figure 2. View of the attenuated total reflectance sampling accessory used to obtain FTIR spectra of the portion of stamp surface directly under the pressure clamp. In the illustration, the stamp has actually been mounted upside down in order to demonstrate the small spot size studied in each measurement.

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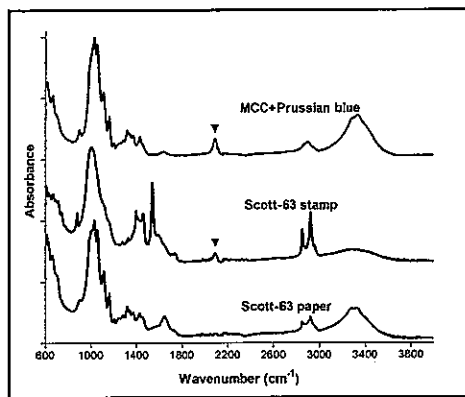


Figure 3. Infrared absorption spectrum for the non-printed region of the Figure 1 pair, the FTIR spectrum of the blue printed region of the pair, and the FTIR spectrum obtained for a 10% physical blend of Prussian blue in microcrystalline cellulose. Arrows mark the position of the diagnostic Prussian blue peak.

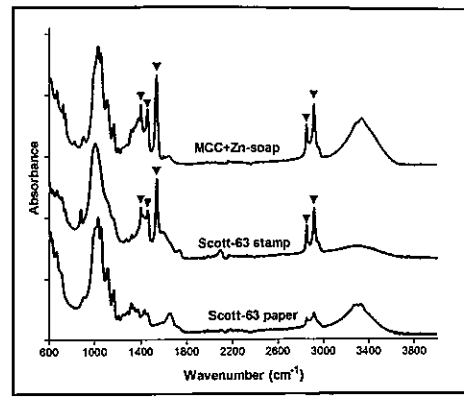


Figure 4. Infrared absorption spectrum for the non-printed paper region of the Figure 1 pair, the FTIR spectrum of the blue printed region, and the FTIR spectrum obtained for a 50% physical blend of zinc soap in microcrystalline cellulose. Arrows mark the positions of the diagnostic zinc soap peaks.

While the presence of Prussian blue in the ink was easily established, the FTIR spectrum of the stamp surfaces contains a number of additional peaks whose origins are not so easily identified. In particular, significant peaks were observed at 872, 1396, 1410, 1456, and 1537 wavenumbers. However, extensive study revealed that many of these peaks could be identified as being due to the presence of either known ink pigments, or with substances used to modify the color of a printing ink.

Initial guidance to the identity of these FTIR peaks was obtained through the use of X-ray fluorescence analysis (XRF).⁸ This study demonstrated that among other elements, the surface of the Scott 63 stamp contained large amounts of a zinc compound, suggesting that the ink formulators used zinc oxide as a whitener. However, the situation must be more complicated than that, since zinc oxide itself does not exhibit any significant absorption bands in its FTIR spectrum.

However, it is known that zinc oxide is a basic metal oxide, and it is also known that basic metal oxides will react with surfactants (such as soap) to produce a metal soap product. For example, basic lead oxide has been shown to react with components in linseed oil to yield a lead soap product.⁹ This suggested that the zinc oxide component in the ink might undergo a similar reaction with the soap used as a surfactant in the oil component of the ink formulation. To evaluate this possibility, a zinc soap was synthesized by the reaction of hydrated zinc oxide with a water dispersion of Ivory soap. The resulting product was blended into microcrystalline cellulose (MCC, discussed further below). Figure 4 shows the FTIR spectrum of this blend together with the FTIR spectrum of the Scott 63 pair.

It is very clear from Figure 4 that the peaks at 1396, 1456, and 1537 wavenumbers in the FTIR spectrum of the Scott 63 pair have corresponding peaks in the FTIR spectrum of zinc soap blended into MCC at an approximate 50 percent level. In addition, the FTIR spectrum of the MCC zinc soap blend also exhibits strong hydrocarbon absorption bands at the same 2849 and 2916 wavenumbers as observed in the FTIR spectrum of the Scott 63 pair. All these features are designated by small arrows in Figure 4.

While the presence of zinc soap in the ink of the Scott 63 pair permits an assignment of most of the key bands in the FTIR spectrum of the Scott 63 stamp surface, its presence



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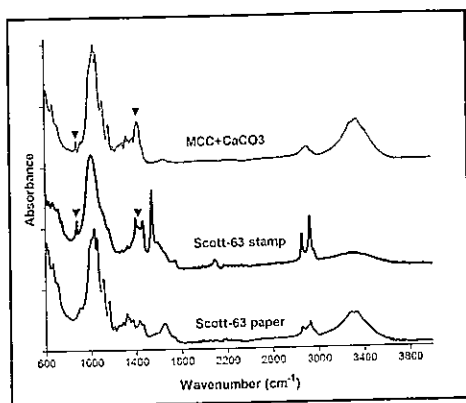


Figure 5. Infrared absorption spectrum for the paper region of the Figure 1 pair, the FTIR spectrum of the blue printed region of the Figure 1 pair, and the FTIR spectrum for a 15 percent blend of calcium carbonate in microcrystalline cellulose. Arrows mark the positions of the diagnostic calcium carbonate peaks.

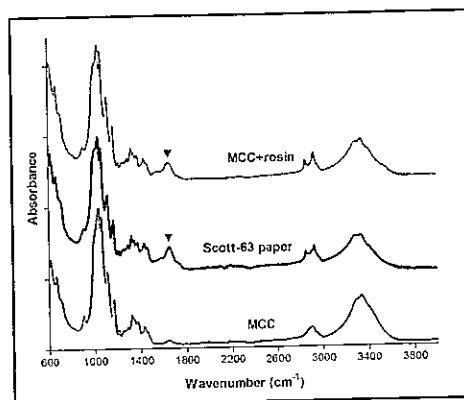


Figure 7. Infrared absorption spectrum of microcrystalline cellulose, the FTIR spectrum obtained for the non-printed region of the Figure 1 pair, and the FTIR spectrum obtained for a 10 percent blend of powdered cherry rosin in microcrystalline cellulose. Arrows mark the diagnostic rosin peaks.

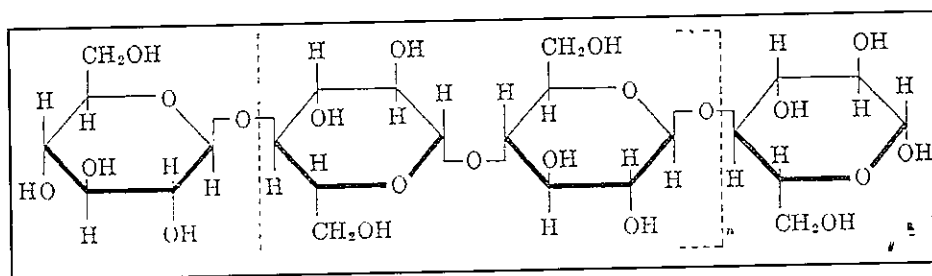
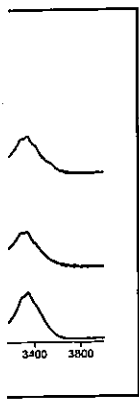


Figure 6. Structure of cellulose. While not explicitly drawn out, the six apices in each ring are meant to denote the presence of carbon atoms.

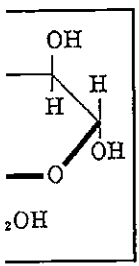
does not enable an assignment of the peaks at 872 and 1410 wavenumbers. However, the energy of these bands certainly identifies them as being due to the presence of a carbonate compound, and the XRF analysis demonstrated the presence of calcium in the stamp surface. From these observations, it was concluded that the FTIR peaks at 872 and 1410 wavenumbers signify the presence of calcium carbonate in the ink layer on the stamp surface. The comparison of FTIR spectra shown in Figure 5 confirms this assignment.

Study of the paper used in printing of the Scott 63 stamps

In the first half of the 19th century, the predominant source of papermaking fibers was linen and cotton rags. The production of paper from wood pulp was not widespread until later in the century.¹⁰ Collected rags were cleaned as well as could be, cut into small pieces 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. These fibers consisted entirely of cellulose,¹¹ which is essentially nothing more than a long-chain carbohydrate (as shown in Figure 6), formed by the polymerization of glucose units. What is important to note about the structure of cellulose is that each glucose unit contains four hydroxyl ($-OH$) and a number of hydrocarbon ($-CH$) bonds.



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A very similar process is used today to produce microcrystalline cellulose (MCC), a substance which has found extensive use as a non-active ingredient in pharmaceutical tablet formulations.¹² To make MCC, one starts with purified cotton and treats this with dilute solutions of mineral acids. The intermediate product is purified, 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 and of cellulose derivatives.¹³ The crystalline domains in cellulose have been classified into four main categories,¹⁴ and native cellulose is usually obtained as a mixture of lattice types I α and I β .¹⁵

Figure 7 contrasts the FTIR spectrum of pharmaceutical grade MCC with the FTIR spectrum obtained from the unprinted region between the stamps illustrated in Figure 1. Since paper and MCC consist largely of cellulose, it is not surprising that the dominant feature in their FTIR spectrum is the broad band at approximately 1025 wavenumbers (which is due to the overlapping bending mode vibrations of the cellulosic hydroxyl vibrational modes). The other dominant feature in the FTIR spectra is the broad absorbance at approximately 3330 wavenumbers, attributable to the stretching mode vibrations of the cellulosic hydroxyl groups. The weaker feature at approximately 2900 wavenumbers is due to the stretching mode vibrations of the cellulosic hydrocarbon groups.

Figure 7 shows that very little difference exists between the FTIR spectrum of the Scott 63 stamp paper and that of MCC. This finding is not surprising considering the similarities in the methods of preparation, and therefore enables the use of MCC as a model compound. A protocol has been developed where in order to prove the existence of a particular chemical compound in the ink of a stamp, one blends a suitable reference compound into MCC and obtains its FTIR spectrum. The presence of this particular compound in the ink of the stamp is verified if the FTIR spectral features characteristic of the reference can be observed in the FTIR spectrum of the stamp.

For example, an absorption band at 1648 wavenumbers is clearly evident in the FTIR spectrum of the stamp paper but is not present in the FTIR spectrum of MCC. The energy of this band identifies it as being due to the presence of neutralized carbonyl groups. In addition, the presence of additional aliphatic hydrocarbon components in the paper is also evident by their characteristic absorption bands at 2849 and 2916 wavenumbers that are due to the symmetric and asymmetric carbon-hydrogen stretching vibrational modes.

After a bit of trial and error, and consultation with the literature, the 1648 wavenumber band was eventually identified as being due to the presence of rosin (a commonly used sizing agent) in the paper. This conclusion was deduced by the equivalence in FTIR spectrum of the Scott 63 paper and the FTIR spectrum obtained for a physical blend of approximately 10% of powdered cherry rosin into MCC (specifically, Avicel grade PH 101). As evident in Figure 7, the equivalence of the FTIR spectrum of the stamp paper and the FTIR spectrum of the MCC/rosin blend is taken as assignment for the 1648 wavenumber feature. It is further to be noted that the addition of rosin to MCC yields the additional hydrocarbon absorption bands 2849 and 2916 wavenumbers.

Conclusion

The forensic analysis of 1¢ blue Benjamin Franklin stamps of the 1861 design has revealed a number of interesting features: The blue pigment in the ink used to print the images on the stamps consisted solely of Prussian blue. The intense blue color of this pigment was softened by the inclusion of two white pigments: primarily zinc oxide, but also with a small amount of calcium carbonate. The surfactant in the processing oil apparently reacted with some of the zinc oxide, producing a zinc soap product. The paper on which the Scott 63 stamps were printed consisted primarily of cellulose that would have been derived from

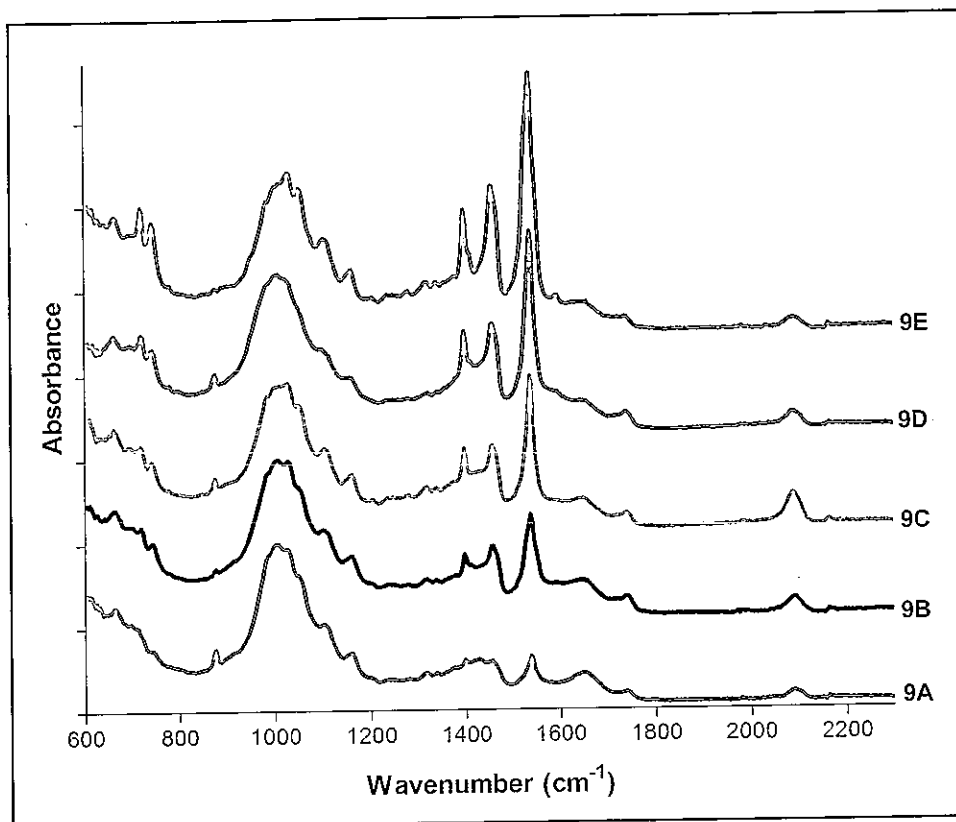
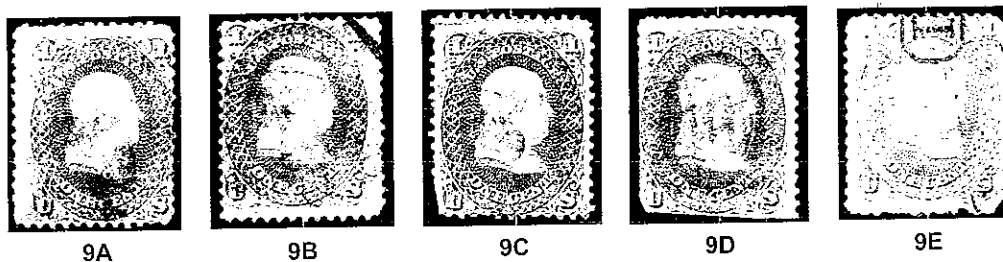


Figure 8. Infrared absorption spectra of the stamps shown in Figures 9A-9E, illustrating the varying proportions of ink components noted among the analyzed stamps.



Figures 9A-9E. 1¢ 1861 stamps of slightly different shades, which correspond to the spectra shown in Figure 8.

cotton fibers. The paper was sized using rosin alone, as no evidence for the presence of alum (another common sizing agent) could be detected.

While the composition of the ink used to print the 1¢ 1861 Franklin stamps is now established, it is important to note that the actual ratios of Prussian blue, calcium carbonate, and zinc soap in the ink were found to vary widely among the stamps studied. Some of the observed variations are illustrated in Figure 8, and the corresponding stamps are shown in figures 9A-9E, demonstrating that each variation in shade has its own specific signature.

The variation in stamp ink composition demonstrated in Figure 8 strongly suggests that a detailed analysis of the intensity patterns in many more stamps might be able to shed additional light on the various printings of the 1¢ 1861 Franklin stamps. For example, Luff

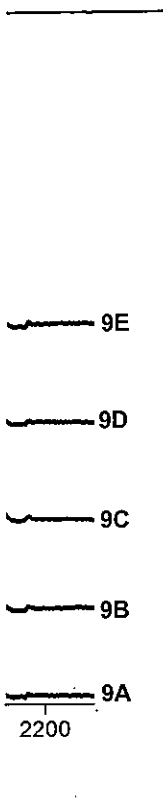
lists ten delivery dates during 1861 for these stamps, and yearly totals for the remainder of the printings.¹⁶ This latter aspect of the project is ongoing as more subjects are collected for analysis, and it is anticipated that results will be reported at a later date.

Acknowledgements

I would like to thank Thomas Lera, Winton M. Blount Chair in Research, of the Smithsonian National Postal Museum, for conducting the X-ray fluorescence analysis on one of the stamps, as well as for his critical reading of this paper prior to publication. I would also like to acknowledge the input of my manuscript review committee, Thomas Lera, John Barwis, Patricia A. Kaufmann and James Allen, for their helpful comments.

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