

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

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**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*

(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



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.

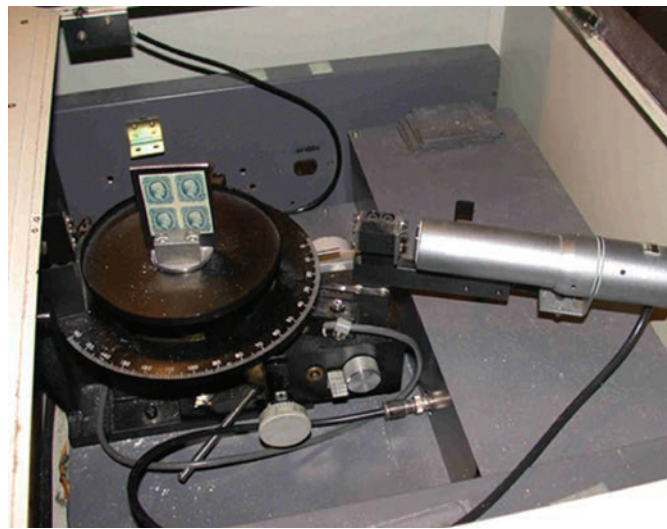
The basis for the XRD effect lies in the fact that the three-dimensional pattern of atoms or molecules in a crystalline solid is such that it can act as a diffraction grating to light (i.e., X-rays) having wavelengths of the same order of magnitude as the spacings between planes of atoms or molecules 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  $\theta$ ) 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,  $\lambda$  is the wavelength of the incident X-ray beam,  $d$  is the distance between planes in the crystal, and  $\theta$  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



**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.

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.

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  $K\alpha$  emission of copper ( $1.54184 \text{ \AA}$ ). As shown in Figure 2, the stamps were pressed against the sample holder in the goniometer and were scanned over the range of  $3.5\text{--}40^\circ 2\theta$  at a scan rate of  $0.5^\circ 2\theta/\text{min}$ . 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  $\text{cm}^{-1}$ , 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 ( $\text{H}_2\text{O}$ ), 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  $\text{cm}^{-1}$ ) where groups of similar atomic masses undergo absorption and the other being termed the “high-frequency” region (2,500–4,000  $\text{cm}^{-1}$ ) 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  $\text{cm}^{-1}$  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  $\text{mm}^2$  area of a stamp and is illustrated in Figure 3.

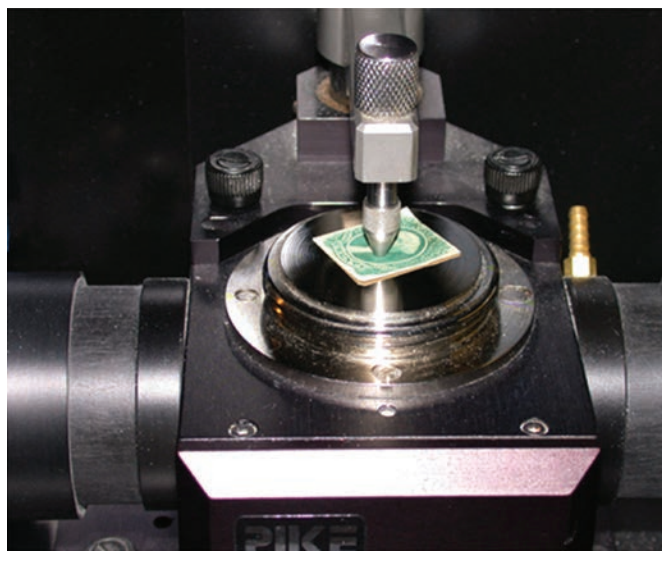


FIGURE 3. View of the attenuated total reflectance sampling accessory used to obtain FTIR spectra of the portion of stamp surface directly under the pressure clamp. In the illustration, the stamp has actually been mounted upside down in order to demonstrate the small spot size studied in each measurement.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

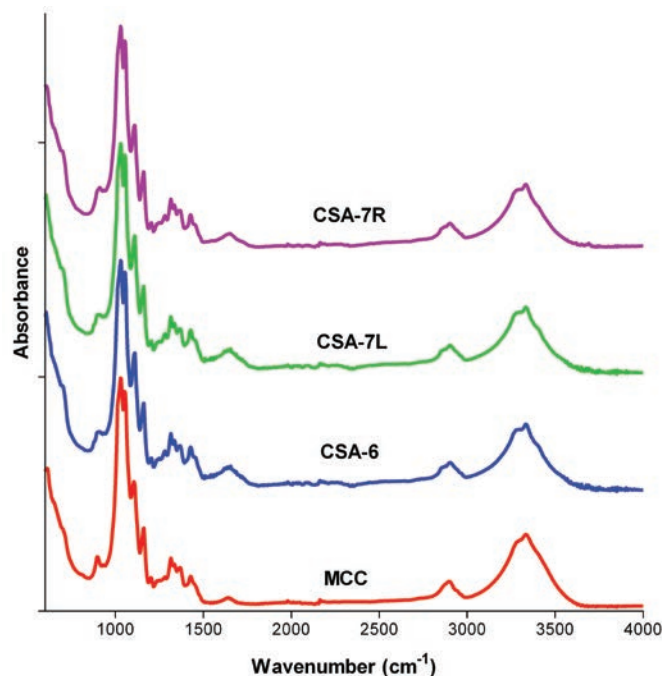


FIGURE 4. Infrared absorption spectra of microcrystalline cellulose and the corresponding FTIR spectra obtained on the margins of the reference stamps. Image used with the permission of *The Confederate Philatelist*.

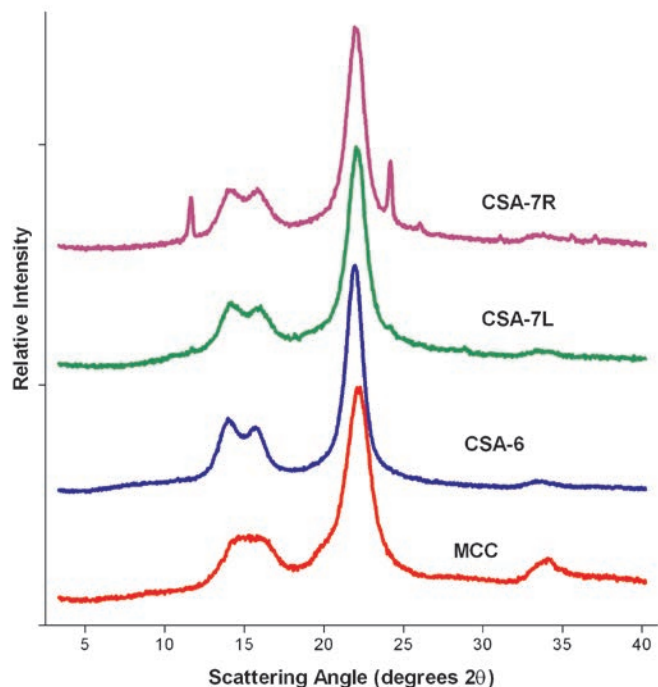


FIGURE 5. X-ray diffraction patterns of microcrystalline cellulose and the corresponding patterns obtained on the margins of the reference stamps. Image used with the permission of *The Confederate Philatelist*.

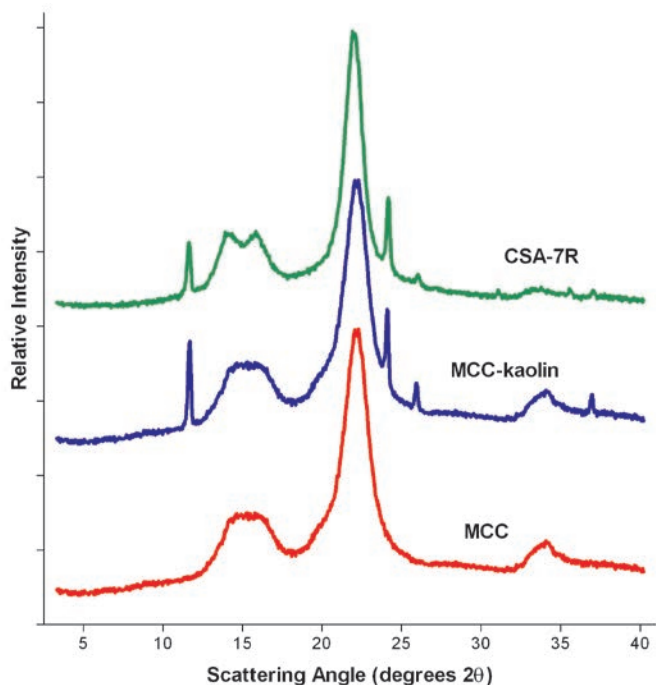


FIGURE 6. X-ray diffraction patterns of microcrystalline cellulose, a 3:7 mixture of MCC and kaolin, and the CSA-7R paper. Image used with the permission of *The Confederate Philatelist*.

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

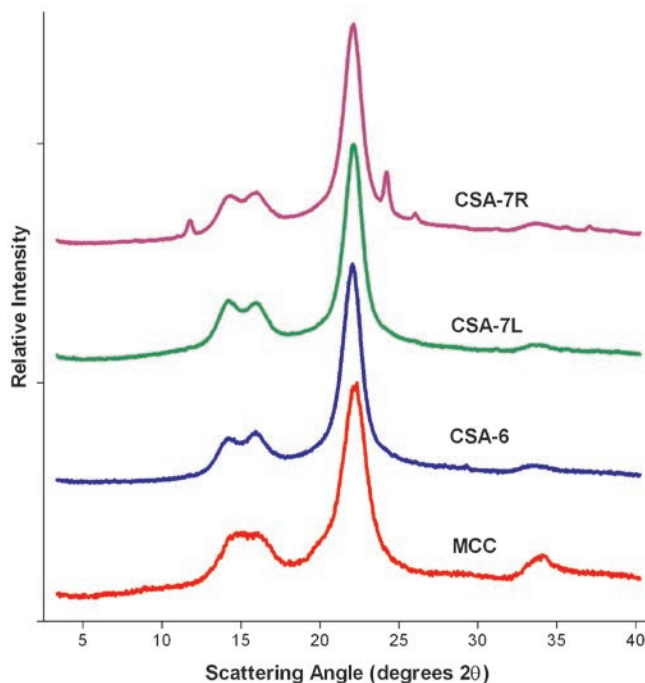


FIGURE 7. X-ray diffraction patterns of microcrystalline cellulose and the corresponding patterns obtained on the faces of the reference stamps. Image used with the permission of *The Confederate Philatelist*.

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  $2,090\text{ cm}^{-1}$ . The energy of this band enables its assignment as being due to the symmetric stretching mode of a cyanide group,

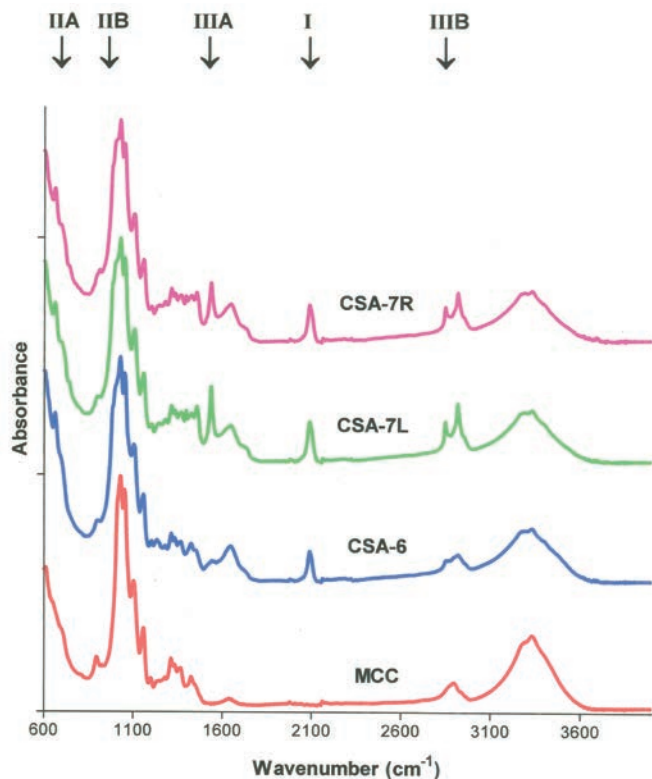


FIGURE 8. Infrared absorption spectra of microcrystalline cellulose and the corresponding FTIR spectra obtained on the faces of the reference stamps with the key analytic regions marked. Image used with the permission of *The Confederate Philatelist*.

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  $\text{FeK}[\text{Fe}(\text{CN})_6]$  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  $665\text{ cm}^{-1}$  and a much broader band at approximately  $1,000\text{ cm}^{-1}$ . 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

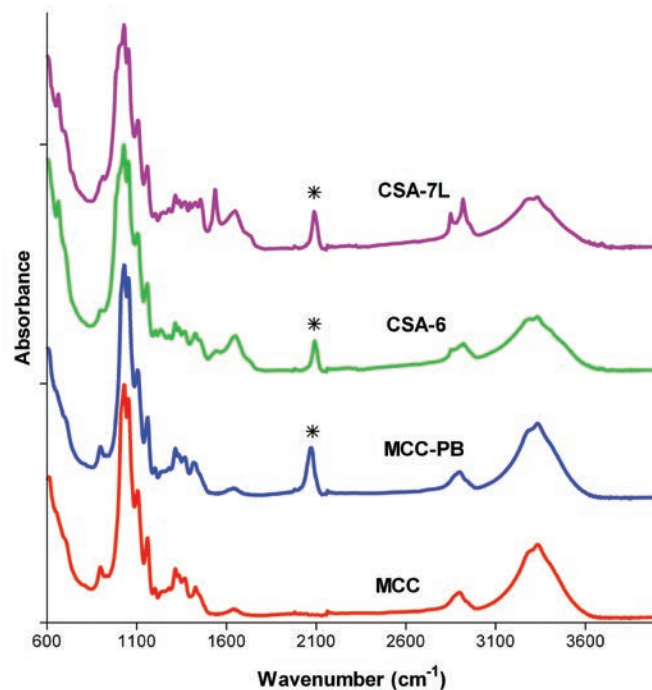


FIGURE 9. Infrared absorption spectra of microcrystalline cellulose, Prussian blue adsorbed onto MCC, and the FTIR spectra obtained on the faces of the CSA-6 and CSA-7L reference stamps. The position of the Prussian blue peak has been marked, and it corresponds to feature I of Figure 8. Image used with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



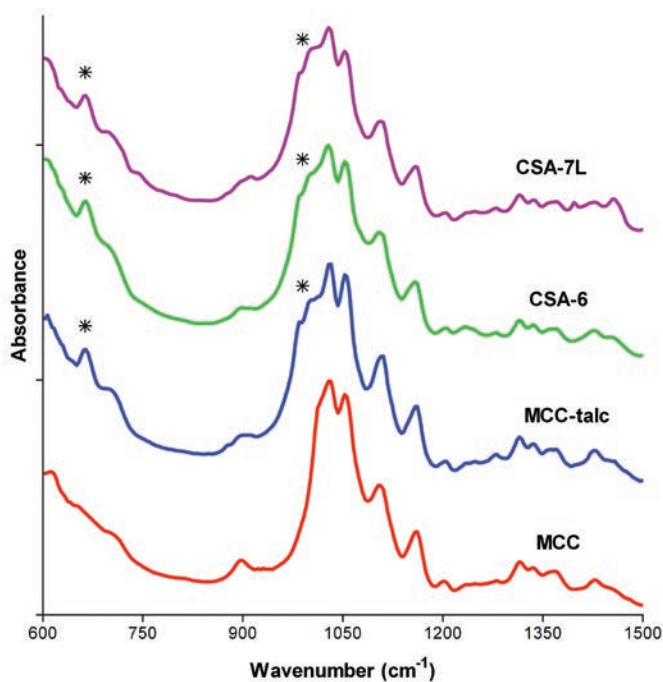


FIGURE 10. Expanded infrared absorption spectra of microcrystalline cellulose, MCC containing talc, and the FTIR spectra obtained on the faces of the CSA-6 and CSA-7L reference stamps. The positions of the talc peaks have been marked, and these correspond to features IIA and IIB of Figure 8. Image used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

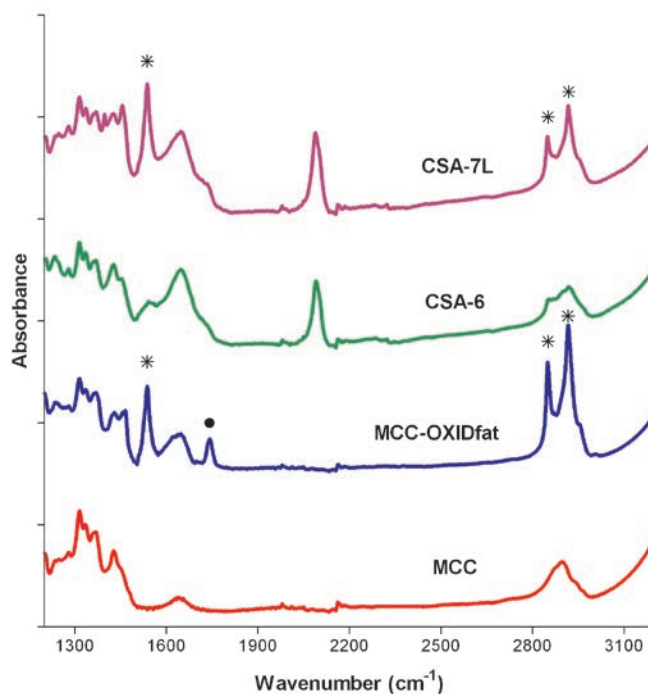


FIGURE 11. Expanded infrared absorption spectra of microcrystalline cellulose, MCC containing oxidized beef fat, and the FTIR spectra obtained from the faces of the CSA-6 and CSA-7L reference stamps. The positions of the talc peaks have been marked, and these correspond to features IIIA and IIIB of Figure 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 ( $1,535\text{ cm}^{-1}$ ) and IIIB ( $2,580$  and  $2,515\text{ cm}^{-1}$ ).

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.



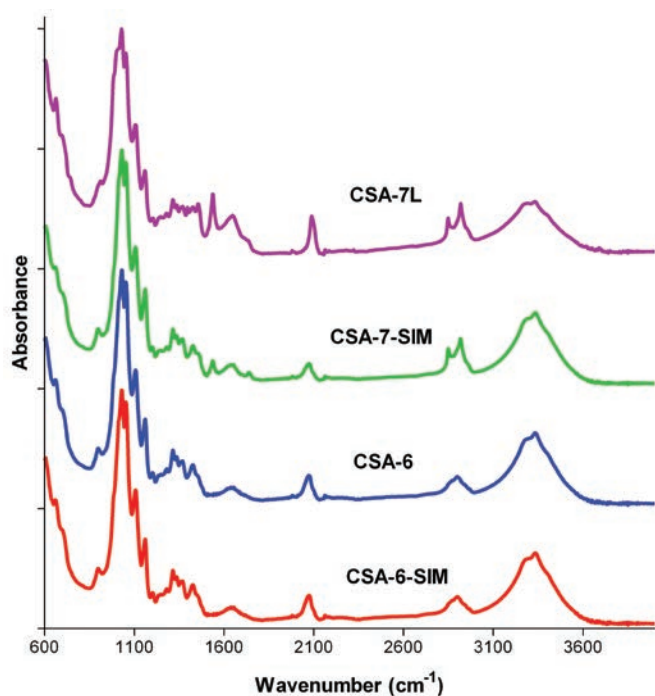


FIGURE 12. Infrared absorption spectrum simulated for a theoretical CSA-6 stamp (obtained by averaging the spectra of MCC containing talc and MCC containing Prussian blue) and the spectrum simulated for a theoretical CSA-7 stamp (obtained by averaging the spectra of MCC containing talc, MCC containing 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

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