A Forensic Study of the Ink and Paper of the Typographed 5-cent Blue Jefferson Davis Stamps Issued by the Confederate States of America

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CSA-6: The “London Print”

- The central motif of the 5-cent blue stamp is a portrait of Jefferson Davis. The stamps were printed from one 400-subject electrotype plate, and were delivered in half sheets of 200 that were further divided by a vertical gutter into two panes of 100 each. The imperforate stamps were printed on thin, white, 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.

Portion of a block from the collection of Jerry Palazolo

CSA-7L: the “Richmond Print” on De La Rue Paper

- Using the De La Rue plates brought through the blockade, more 5-cent stamps were typographed in Richmond, Virginia, and so these stamps are known as the "Richmond Print" issue. The initial printings were made on the thin, white, hard-surface paper that had been imported from England. In addition, the ink used in the printing of the Richmond prints was mixed locally. Since the printing plates were the same as used for the London prints, the format of the sheets is the same.

From the collection of H.G. Brittain

CSA-7R: the “Richmond Print” on Local Paper

- After the De La Rue paper ran out, additional 5-cent stamps were typographed in Richmond, but were printed on an inferior paper that was manufactured locally. These stamps are also known as "Richmond Prints“, and were printed using the same type of locally mixed ink. Since the printing plates were the same as used for the London prints, the format of the sheets is the same.

Portion of a block purchased from Patricia A. Kaufmann

C S I (Confederate Stamp Investigator) Technology

- In this program of study, Infrared (IR) Absorption Spectroscopy, combined with attenuated total reflectance (ATR) sampling is used to study the ink of a stamp.
- In addition, X-Ray Diffraction (XRD) is used to study the paper bearing the ink.
- The general procedure to be followed is to overlay the spectra or diffraction patterns obtained from the stamps with the spectrum or diffraction pattern of a component suspected to be present in the analyzed stamp.

IR Spectroscopy (1)

- The absorption of IR energy causes the atoms in a molecule to become agitated, so they undergo more extensive motion, but do so without destroying the molecule.
- The motions of atoms, or groups of atoms, in a molecule are determined by the identity of the atoms involved and the strength of the bonds holding them together.
- Each pattern of vibrational motion of a molecule results in the appearance of a unique band or peak in its IR spectrum.

IR Spectroscopy (2)

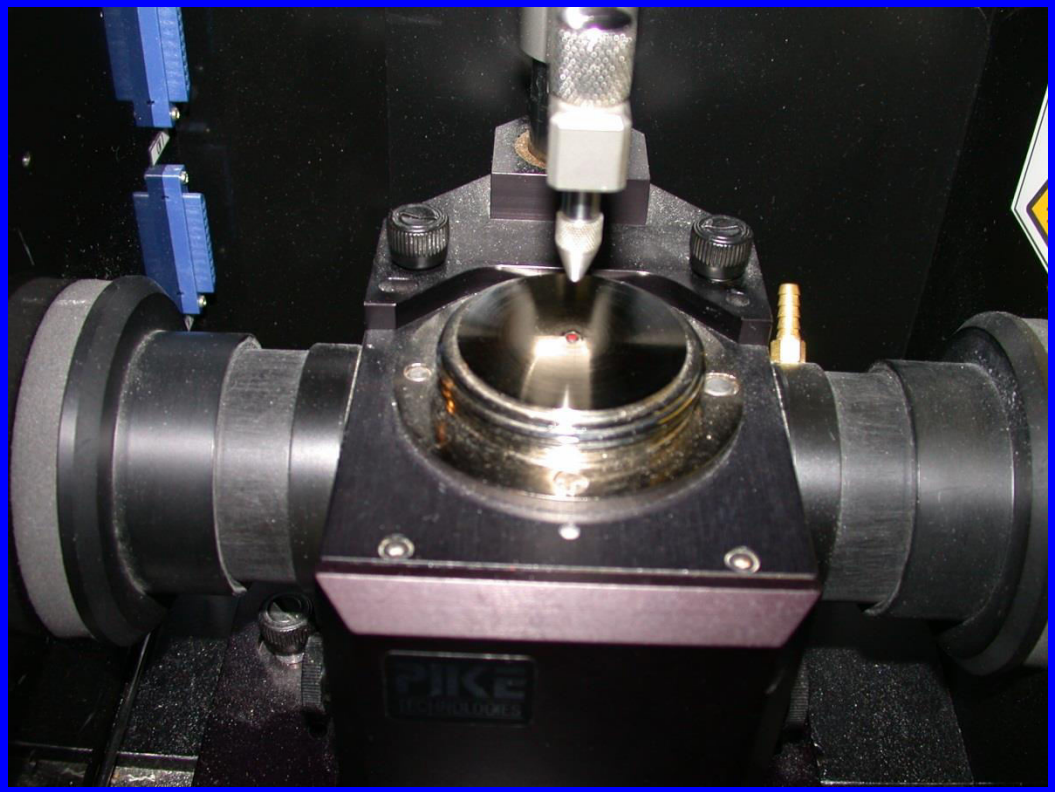
- Thus, an IR spectrum consists of lots of peaks corresponding to lots of molecular vibrational types.
- Since the exact details of the IR spectrum of a substance doing the absorption are determined by the atoms in the molecules and how they are connected, the spectrum is effectively a fingerprint for the absorbing molecule.
- It will be shown that the physical properties of microcrystalline cellulose are effectively the same as that of the 19^{th} century papers, and hence makes a useful reference compound.

IR Spectroscopic Instrumentation (1)

- Infrared absorption spectra were obtained using a Shimadzu model 8400S spectrometer, with the data being acquired using the attenuated total reflectance (ATR) sampling mode.

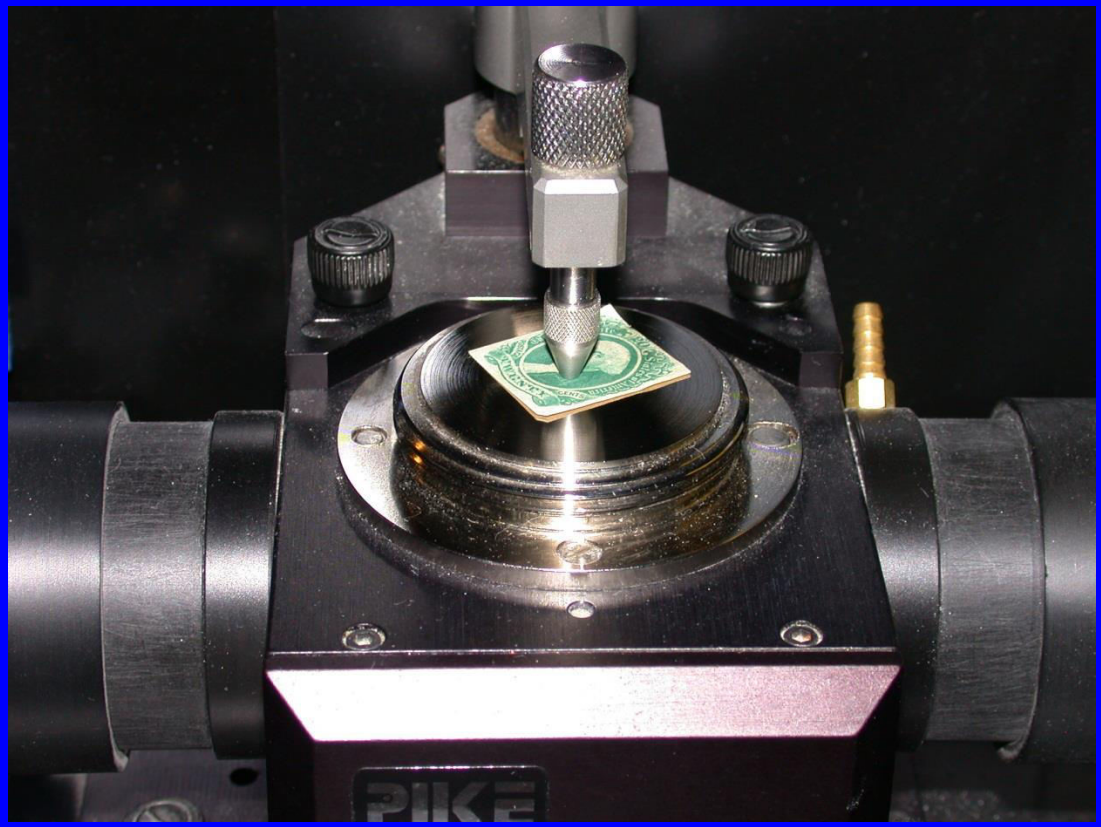
IR Spectroscopic Instrumentation (2)

- The samples were clamped against the ZnSe crystal of a Pike MIRacle™ single reflection horizontal ATR sampling accessory.



IR Spectroscopic Instrumentation (3)

- Configuration of sample measurement by means of attenuated total reflectance IR spectroscopy.



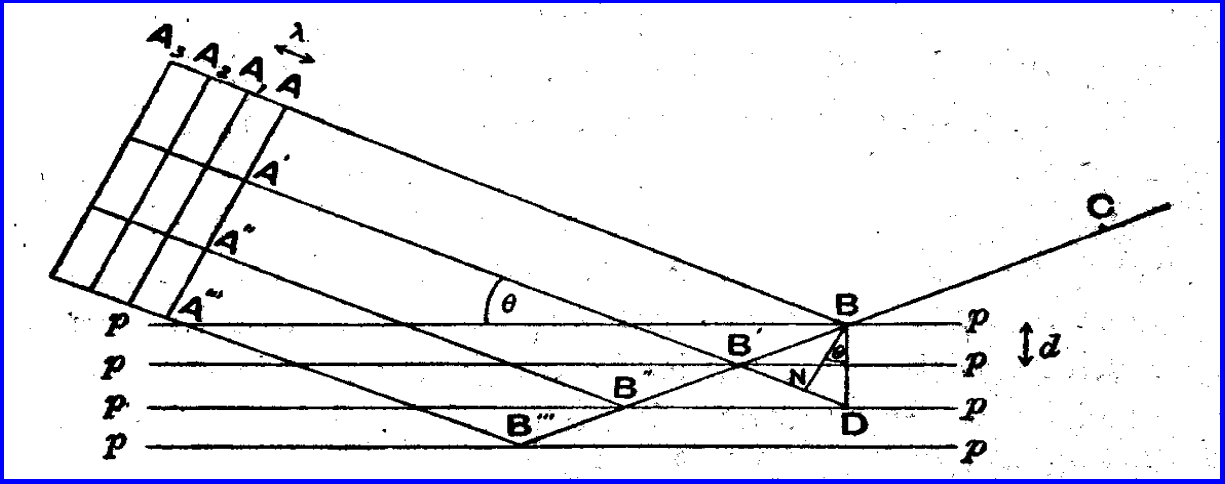
X-Ray Diffraction (1)

- Because the spacing between planes of molecules in crystalline solids is approximately the same as the wavelengths of X-rays, crystals are capable of diffracting X-rays.
- When applied to crystalline powders, the technique is known as X-ray powder diffraction (XRPD).
- Because the XRPD pattern of a substance is derived from its crystal structure, XRPD patterns are also capable of being used for qualitative identification of unknown materials.

X-Ray Diffracton (2)

- Diffraction off the ensemble of surfaces yields information on all possible atomic spacings in the crystal lattice.
- Bragg's Law is used to interpret the data:

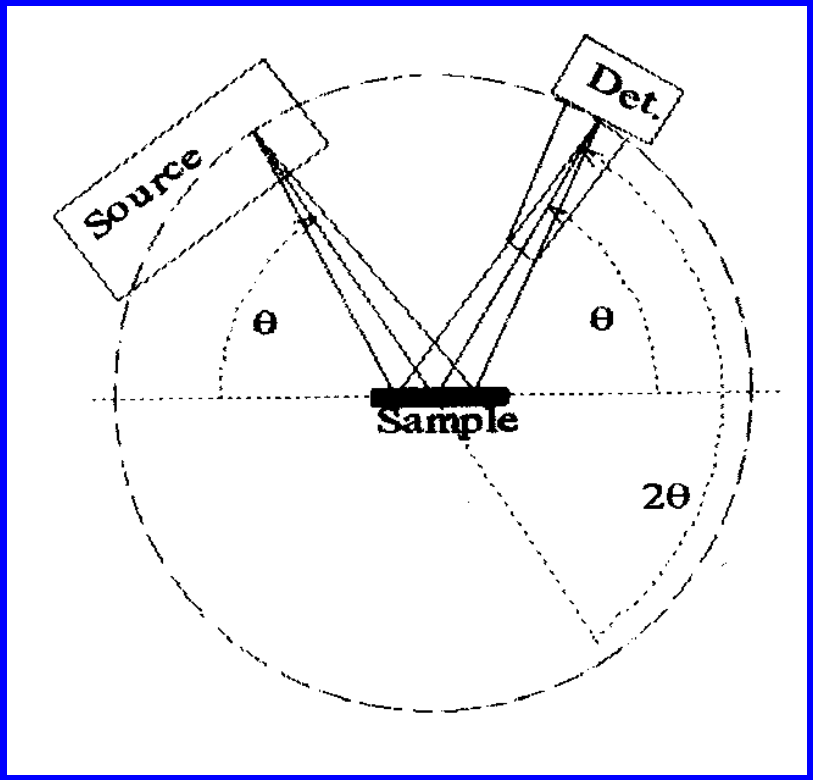
$$n\,\lambda \;=\; 2\,d\,\sin\theta$$



X-Ray Diffraction (3)

Linear Detector Diffractometer

- The sample and the X-ray source are held as a fixed angle to each other, and the detector is swept across the sample surface.

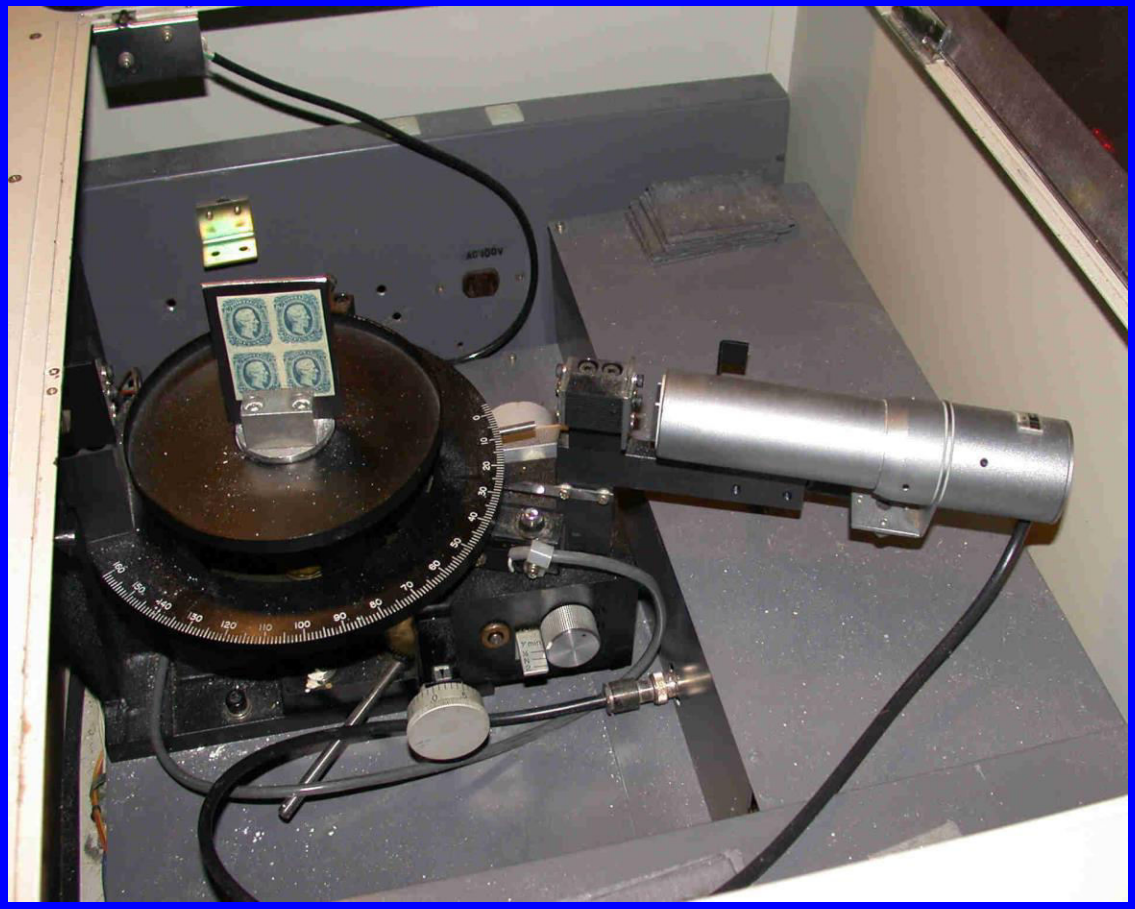


X-Ray Diffraction Instrumentation (1)

- XRPD patterns were obtained using a Rigaku MiniFlex powder diffraction system, equipped with a horizontal goniometer operating in the $\theta/2\theta$ mode. The X-ray source was nickel-filtered Kα emission of copper (1.54184 Å). Stamps were held against the sample holder, and were scanned over the range of 3.5 to 40 degrees 2θ at a scan rate of 0.5 degrees 2θ/min.

X-Ray Diffraction Instrumentation (2)

- The sample is held vertically at a fixed angle to the X-ray source. The detector is rotated between 3 and 40 degrees 2θ with respect to the incident X-ray beam.



Paper Used in the Printing of 19th Century Stamps (1)

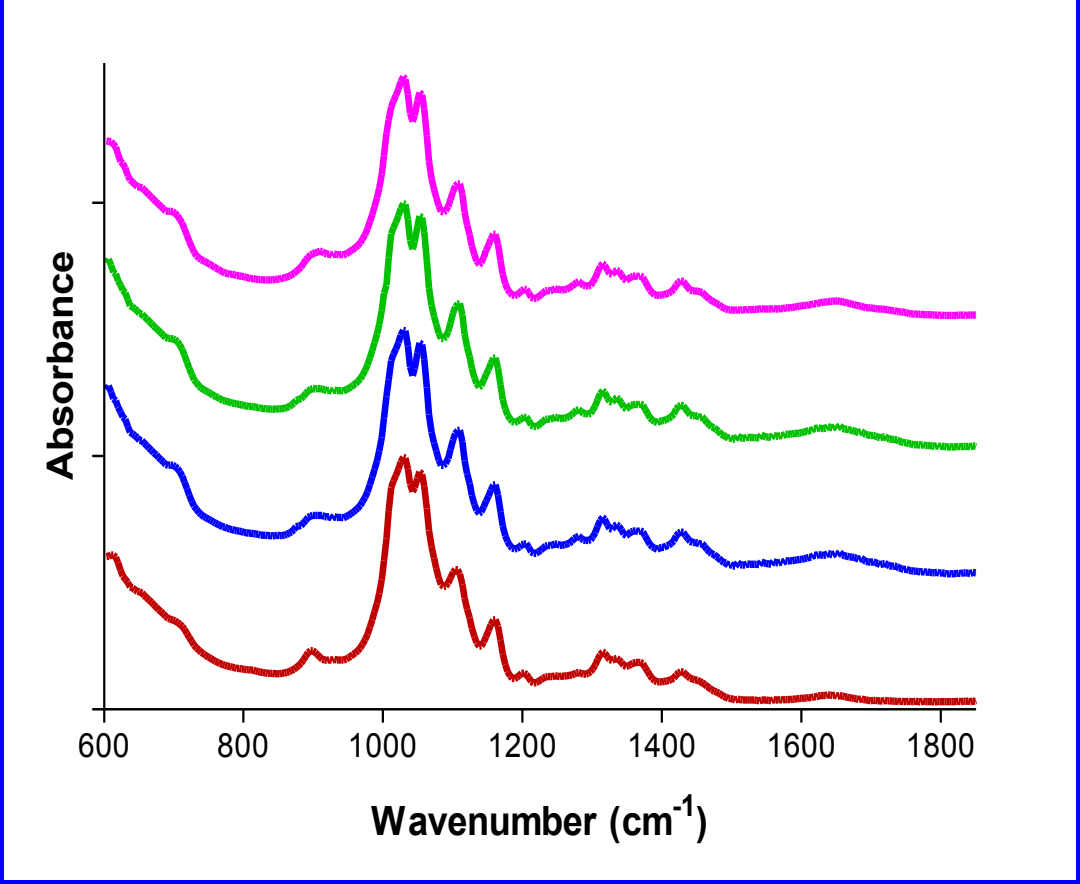
- In the first half of the 19th century, the only source of papermaking fibers was linen and cotton rags.
- Collected rags were cleaned, cut into pieces about 2 to 4 inches square, and then placed in kettles where they were heated with chemicals.
- This process destroyed any coloring and rendered the pieces into a state where they could be pulverized into the component fibers that consist entirely of cellulose.
- The cellulose pulp was mixed with a filler/binder material and then pressed into sheets for drying.

Paper Used in the Printing of 19th Century Stamps (2)

- The filler/binder materials (also known as sizing materials) could be organic (*e.g.*, rosin) or inorganic (*e.g.*, insoluble salts or clays).
- Interestingly, the paper sourced from this time period consists of the same solid-state form of cellulose as the modern pharmaceutical excipient, microcrystalline cellulose (MCC).
- MCC therefore makes an excellent model compound that facilitates the interpretation of forensic results obtained on 19th century stamps.

IR Spectra of Paper: Fingerprint Region

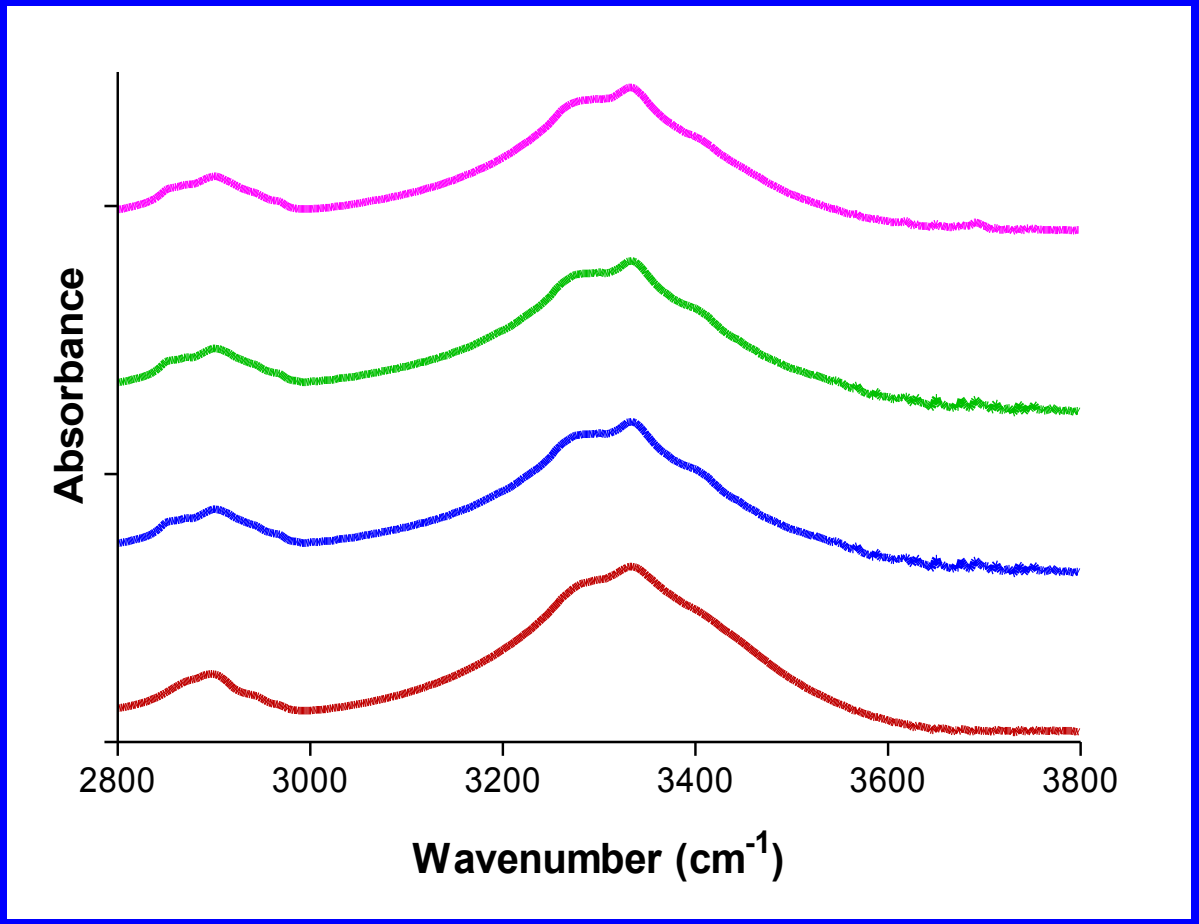
- FTIR spectroscopy in the fingerprint region cannot differentiate between London and Richmond paper.



- Magenta trace = CSA-7R; Richmond paper
- Green trace = CSA-7L; London paper
- Blue trace = CSA-6
- Red trace = microcrystalline cellulose

IR Spectra of Paper: High Frequency Region

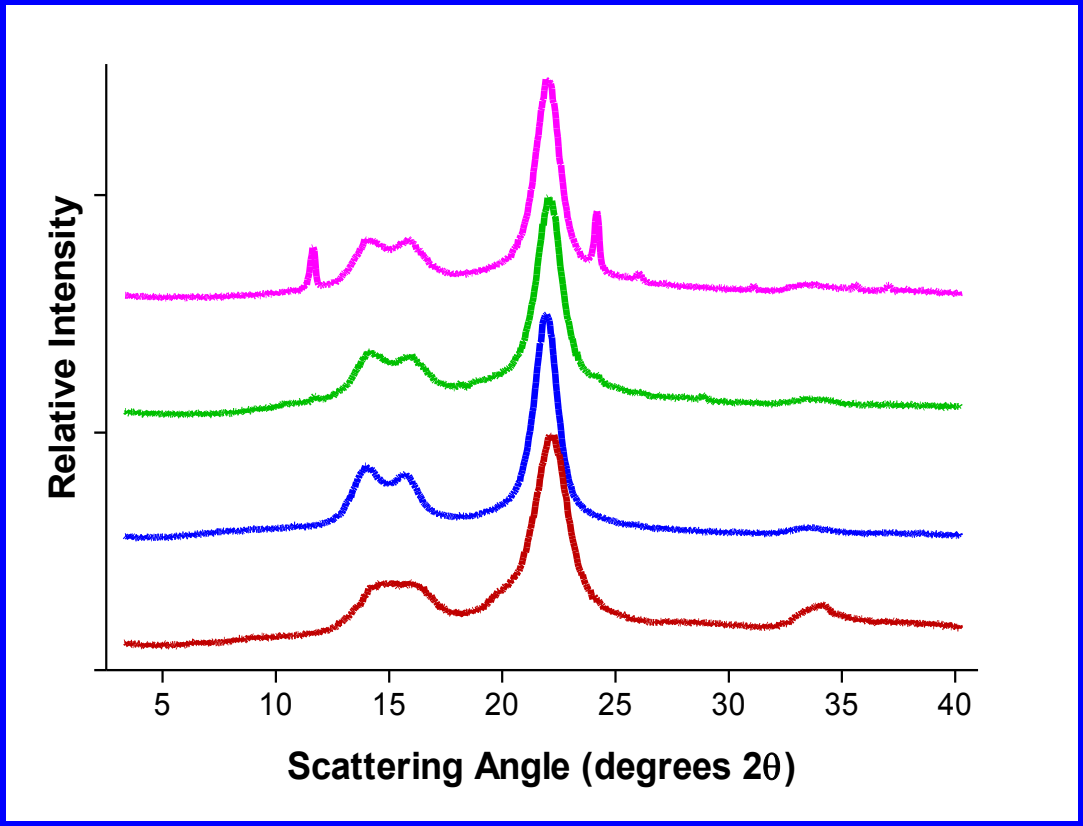
- FTIR spectroscopy in the high frequency region also cannot differentiate between London and Richmond paper.



- Magenta trace = CSA-7R; Richmond paper
- Green trace = CSA-7L; London paper
- Blue trace = CSA-6
- Red trace = microcrystalline cellulose

X-Ray Diffraction of Paper (1)

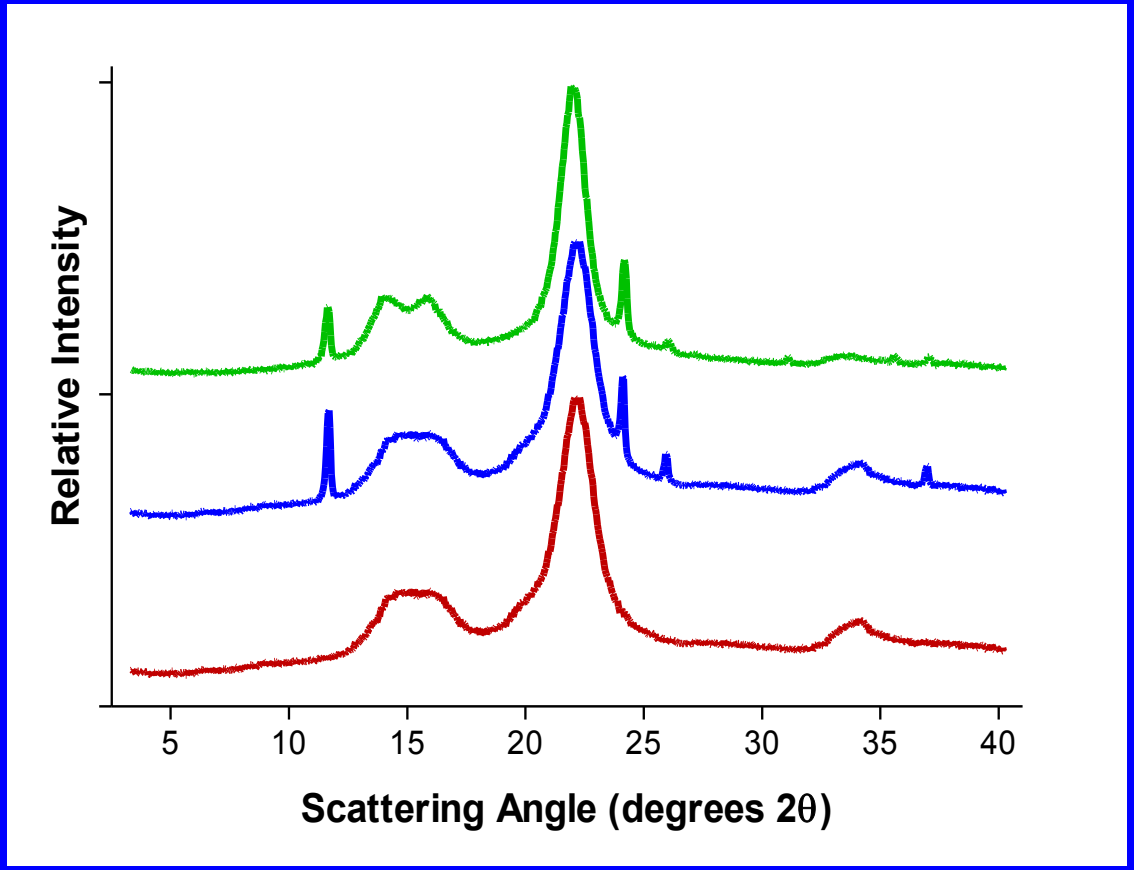
- XRD analysis can differentiate between London and Richmond paper, since the Richmond paper contains a crystalline component (which apparently do not cause absorption in the IR spectrum) that the London paper does not.



- Magenta trace = CSA-7R; Richmond paper
- Green trace = CSA-7L; London paper
- Blue trace = CSA-6
- Red trace = microcrystalline cellulose

X-Ray Diffraction of Paper (2)

- XRD pattern obtained for Richmond paper, and the XRPD pattern obtained on a sample consisting of 70% microcrystalline cellulose and 30% kaolin.



- Green trace = locally sourced Richmond paper
- Blue trace = MCC kaolin physical mixture
- Red trace = Microcrystalline cellulose

Paper Analysis: Conclusions

- The paper sourced from De La Rue consists of the same solid-state form of cellulose as microcrystalline cellulose. Whatever fillers or sizers were used in its manufacture were not crystalline.
- The locally sourced paper used in the Richmond printings contained kaolin clay as the filler/sizer agent.
- X-ray diffraction can be used to distinguish between London paper and Richmond paper on the basis of the presence or absence of the kaolin component.

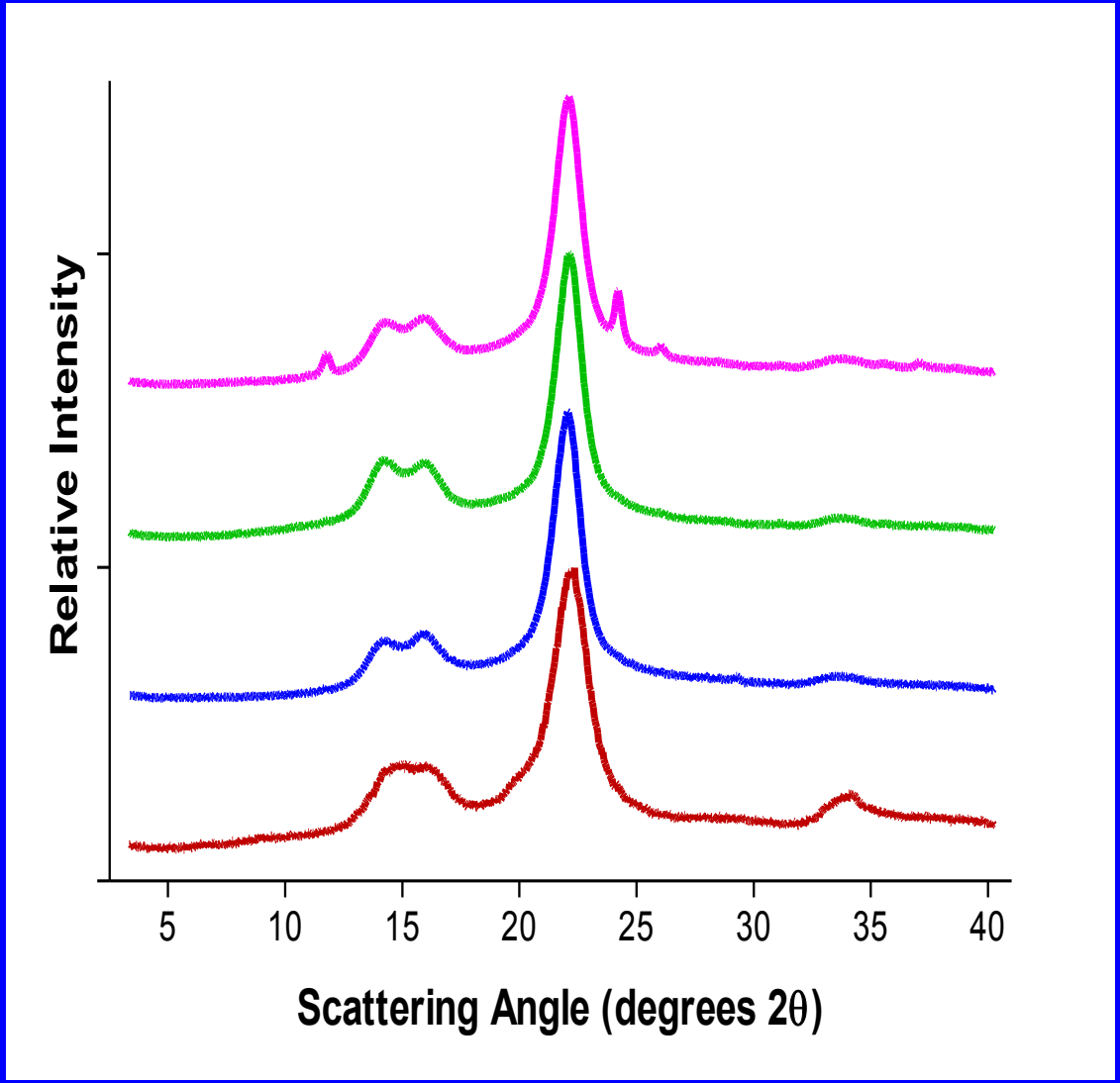
Characteristics of Ink Suitable for Typographic Production of Stamps (1)

- Typography consists of printing from raised characters or plates. The printing of stamps by the Confederacy was conducted one sheet at a time, thus falling into the category of job printing.
- The plates used for typography are produced from an engraved plate, where 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.

Characteristics of Ink Suitable for Typographic Production of Stamps (2)

- Job press inks should possess as heavy a body that the paper stock will permit, and should be almost buttery in nature as possible 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 inks contain oils, their drying is not instantaneous, and it is known that the drying process entails oxidation of the unsaturated groups in the oils.

X-Ray Diffraction of Stamp Surfaces



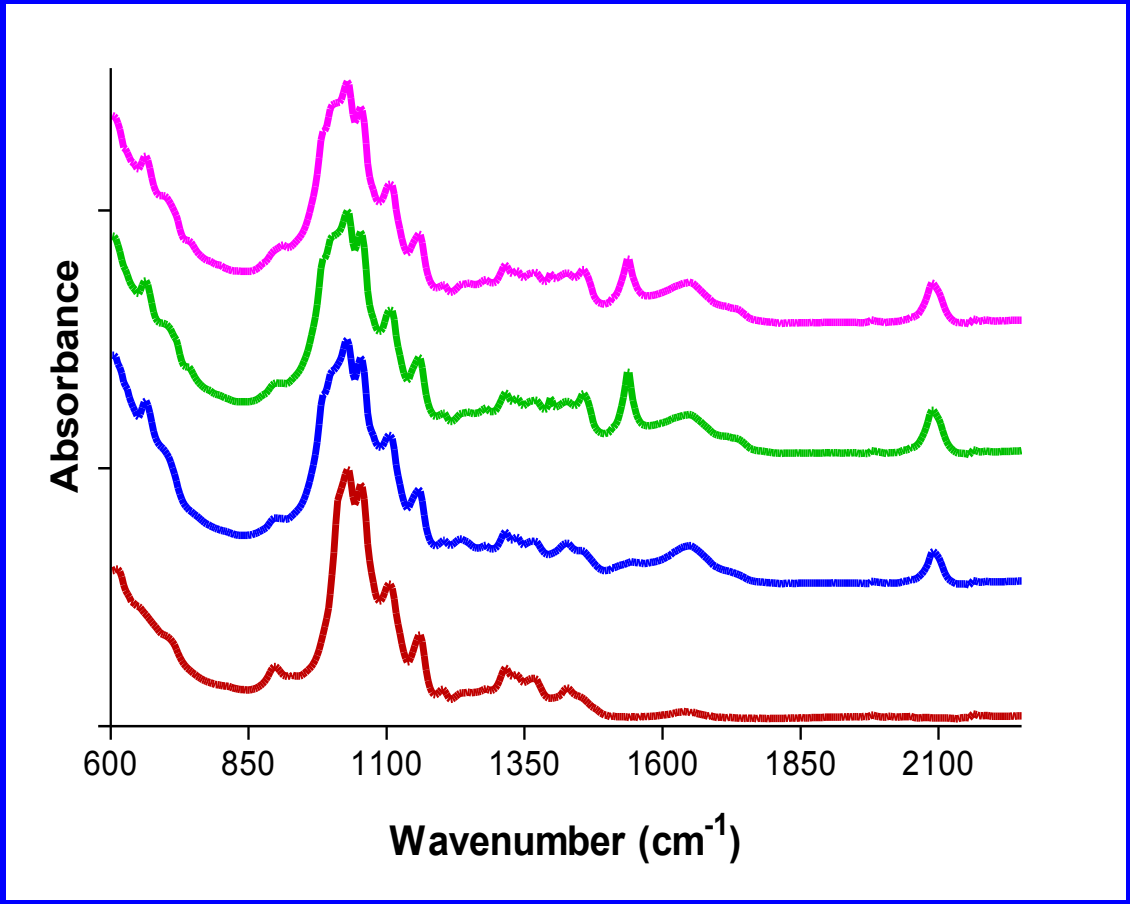
- Magenta trace = CSA-7R; Richmond paper
- Green trace = CSA-7L; London paper
- Blue trace = CSA-6
- Red trace = microcrystalline cellulose

XRD and Stamp Surfaces: Conclusions

- The XRD patterns obtained off the printed surfaces of the CSA-6 and CSA-7 issues are not different from the XRD patterns of the paper used in the printing of these stamps.
- XRD analysis can therefore be used to distinguish between Richmond prints on London paper and Richmond prints on Richmond paper.
- However, XRD analysis cannot be used to distinguish between CSA-6 stamps and the CSA-7 stamps printed on De La Rue paper.

IR Study of Stamps: Fingerprint Region

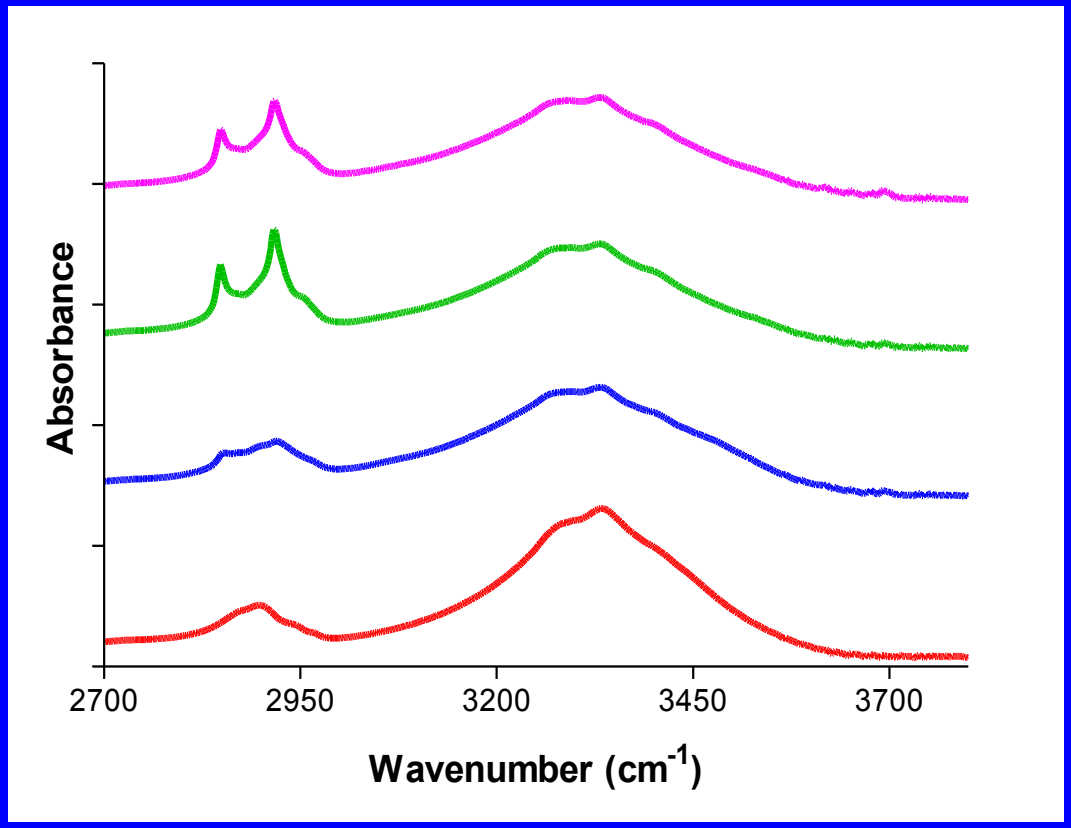
- One can use FTIR spectroscopy in the fingerprint region to distinguish between the ink used for the London printings and the Richmond printings.



- Magenta trace = CSA-7; Richmond paper
- Green trace = CSA-7; London paper
- Blue trace = CSA-6
- Red trace = microcrystalline cellulose

IR Study of Stamps: High Frequency Region

- FTIR spectroscopy in the high frequency region also contains significant differences that serve to distinguish between London and Richmond paper.



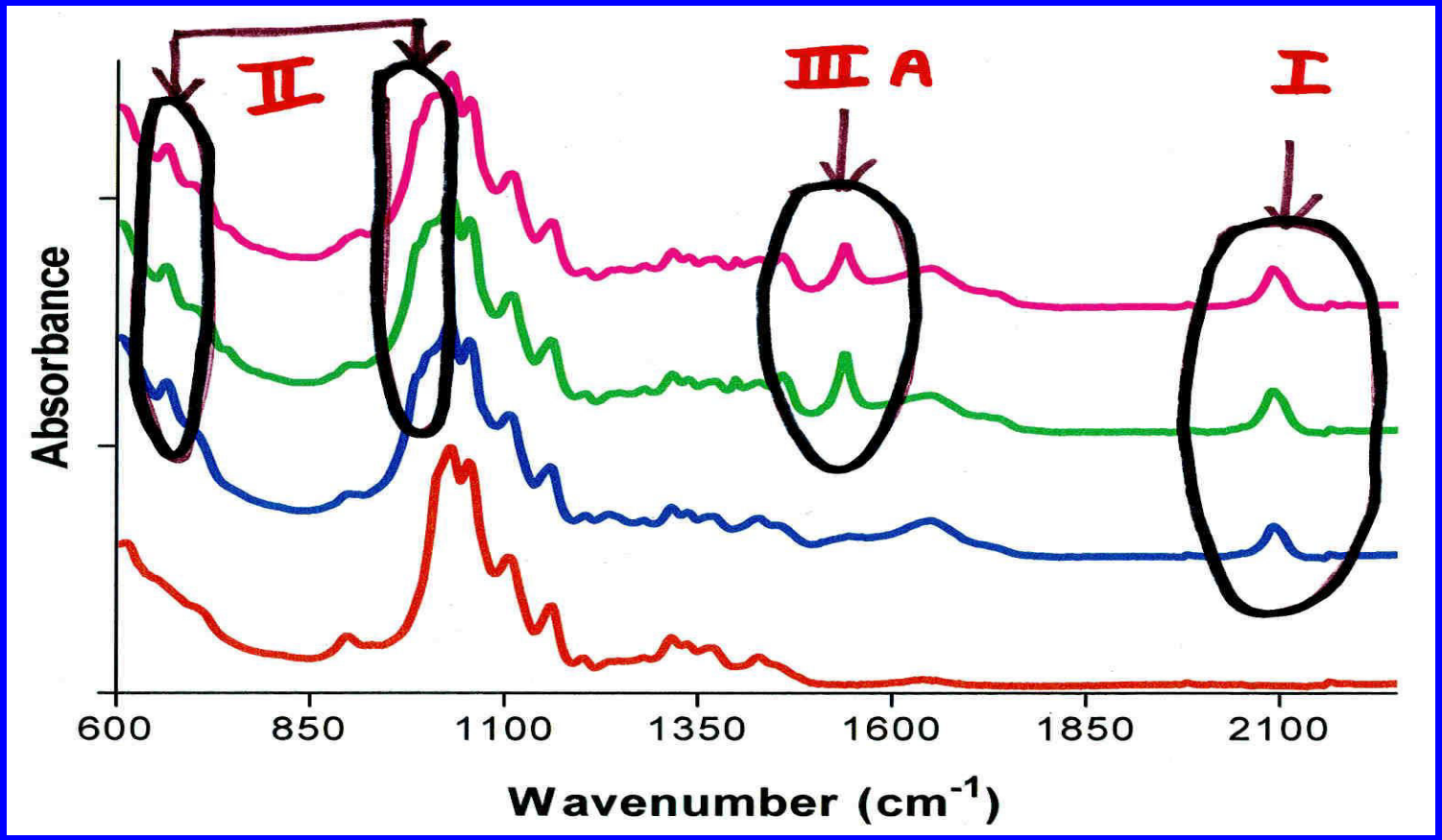
- Magenta trace = CSA-7; Richmond paper
- Green trace = CSA-7; London paper
- Blue trace = CSA-6
- Red trace = microcrystalline cellulose

FTIR Study Conclusions (1)

- The printing ink used for the CSA-6 contains features that enable one to distinguish stamps printed using London ink from stamps printed using Richmond ink.
- The ink used in Richmond to print the CSA-7 stamps on both De La Rue paper and on Richmond paper is the same.

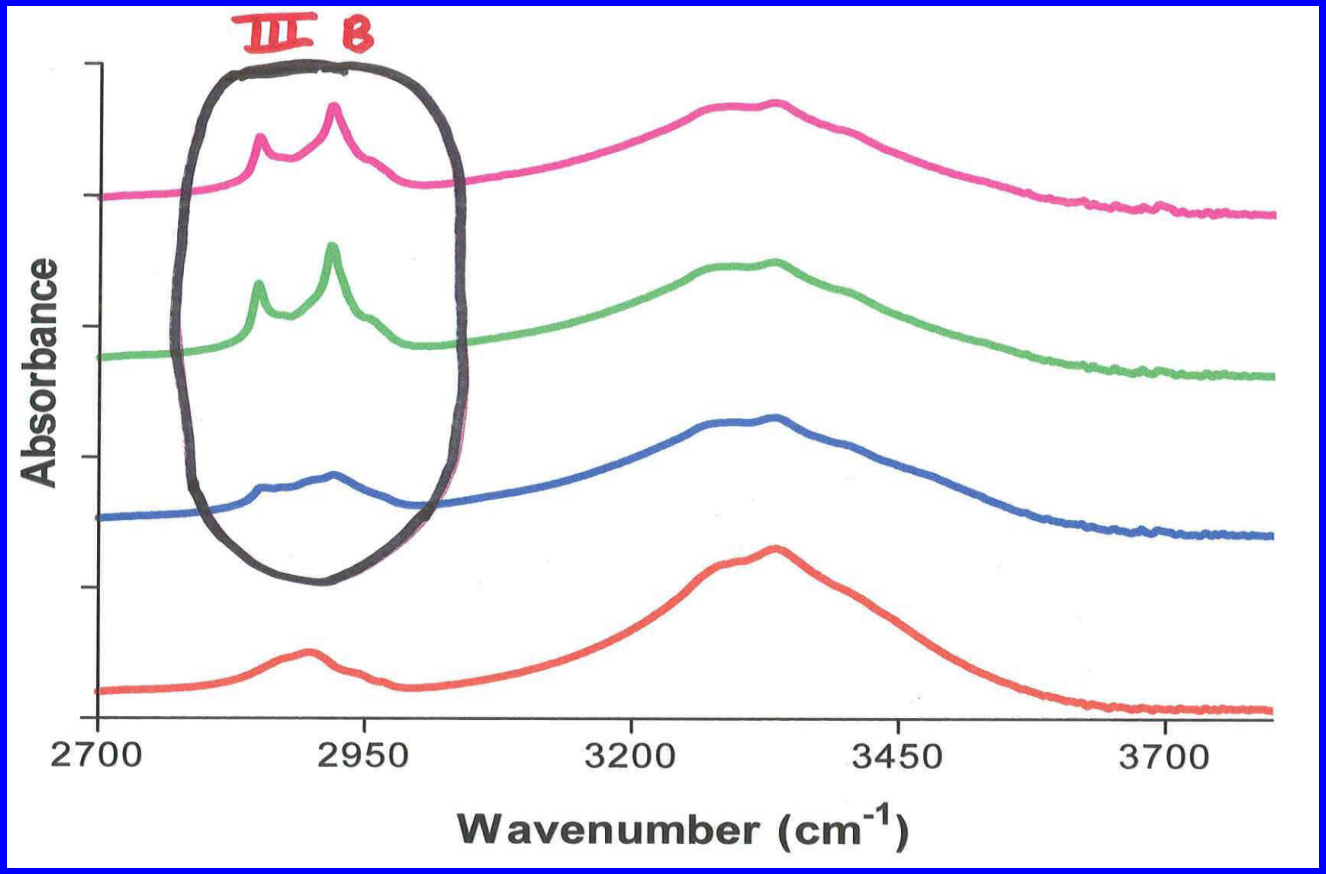
Regions of Importance in the IR Spectra of the CSA-6 and CSA-7 Issues (1)

- Fingerprint region:

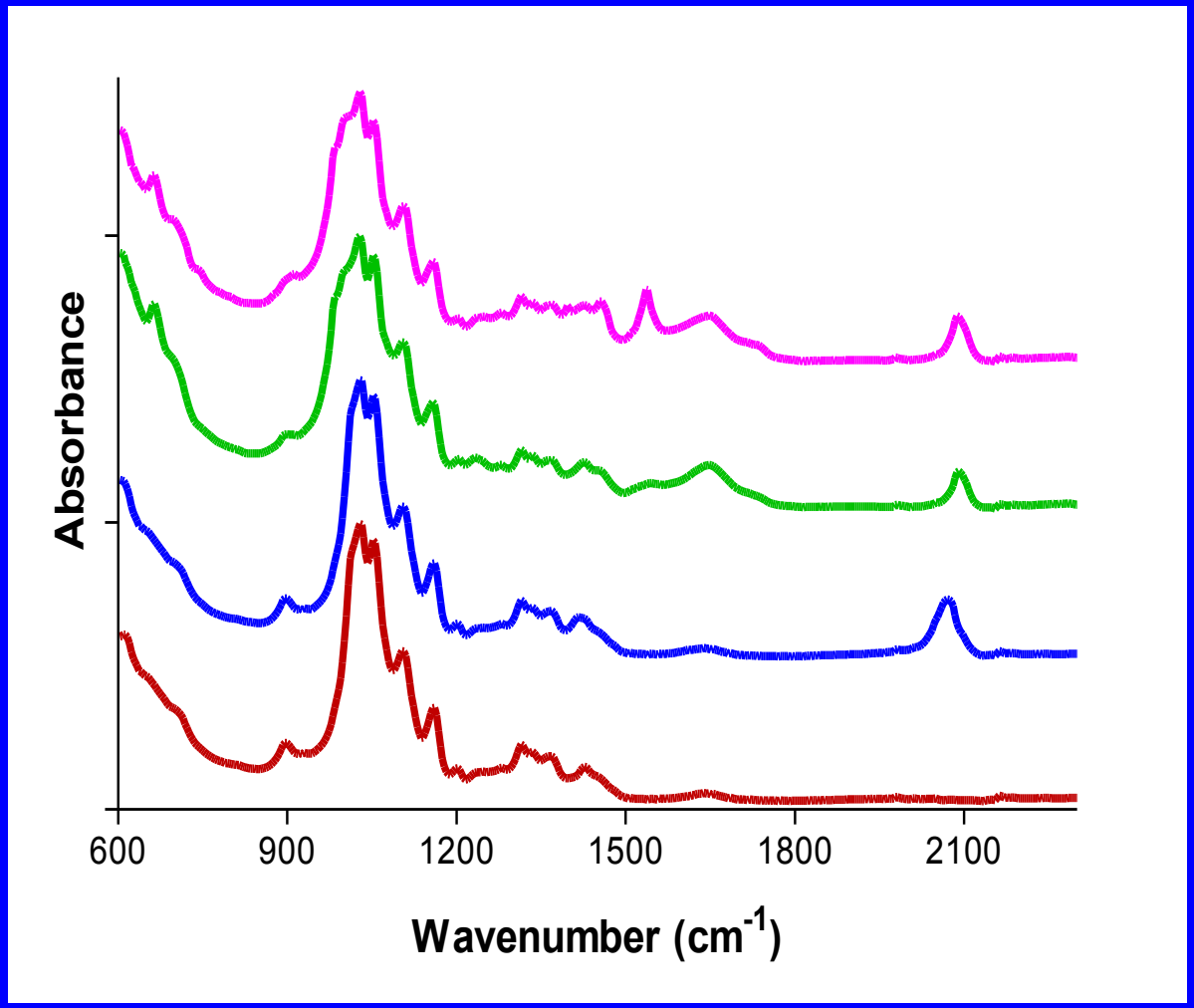


Regions of Importance in the IR Spectra of the CSA-6 and CSA-7 Issues (2)

- High-frequency region:

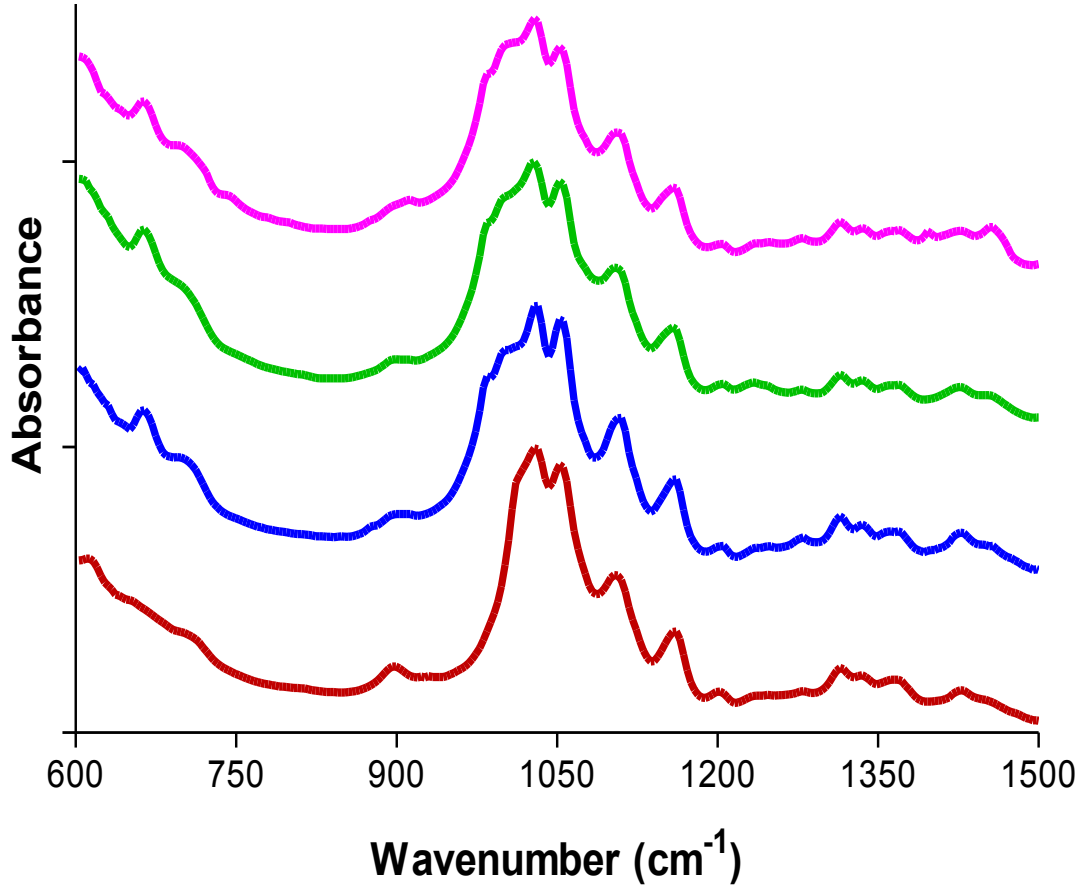


I: IR Spectrum of Prussian blue absorbed onto microcrystalline cellulose



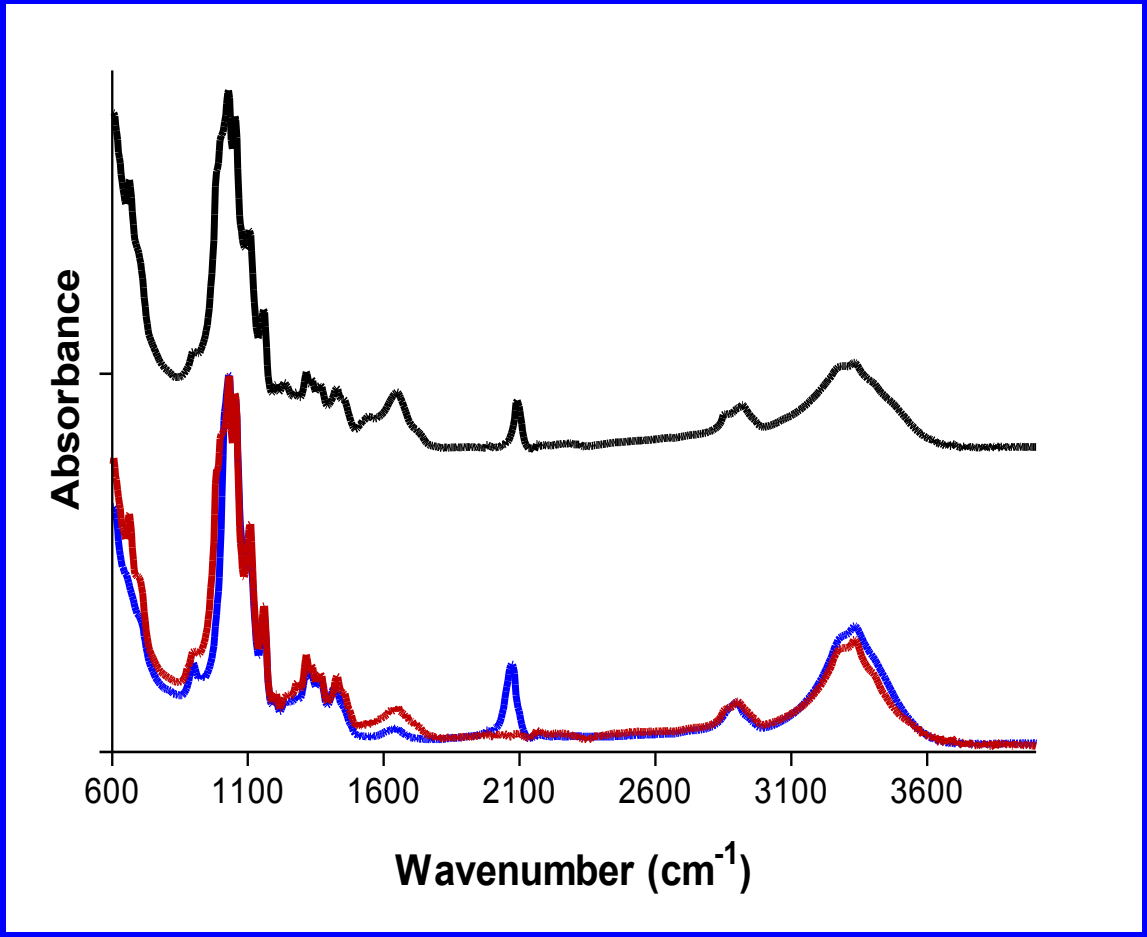
- Magenta trace = CSA-7; Richmond paper
- Green trace = CSA-6
- Blue trace = Prussian blue on MCC
- Red trace = microcrystalline cellulose

II: IR Spectrum of talc wet slurried into microcrystalline cellulose



- Magenta trace = CSA-7; Richmond paper
- Green trace = CSA-6
- Blue trace = Talc in MCC
- Red trace = microcrystalline cellulose

IR Spectral Analysis of CSA-6

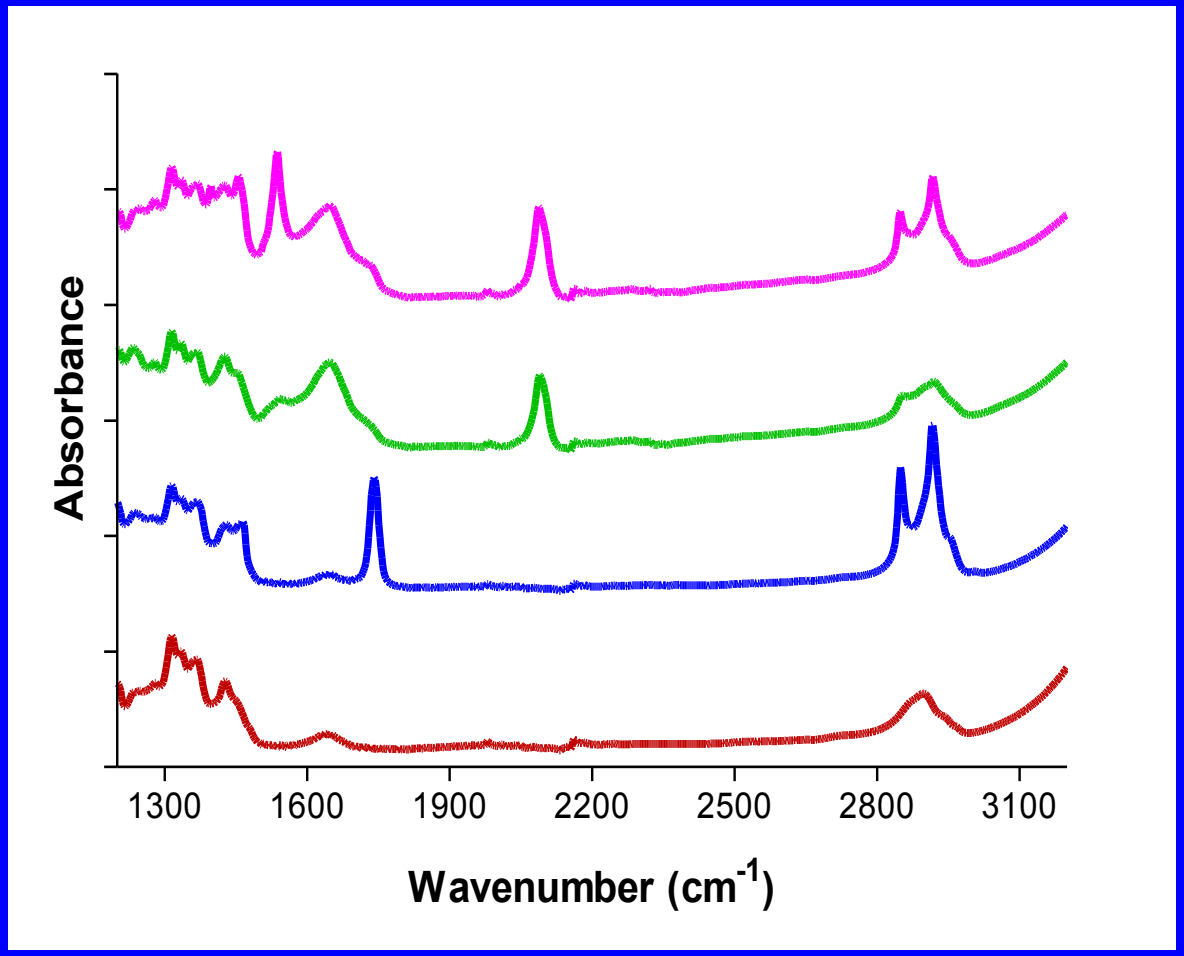


- Black trace = CSA-6
- Blue trace = Prussian Blue in microcrystalline cellulose
- Red trace = Talc in microcrystalline cellulose

FTIR Study Conclusions (2)

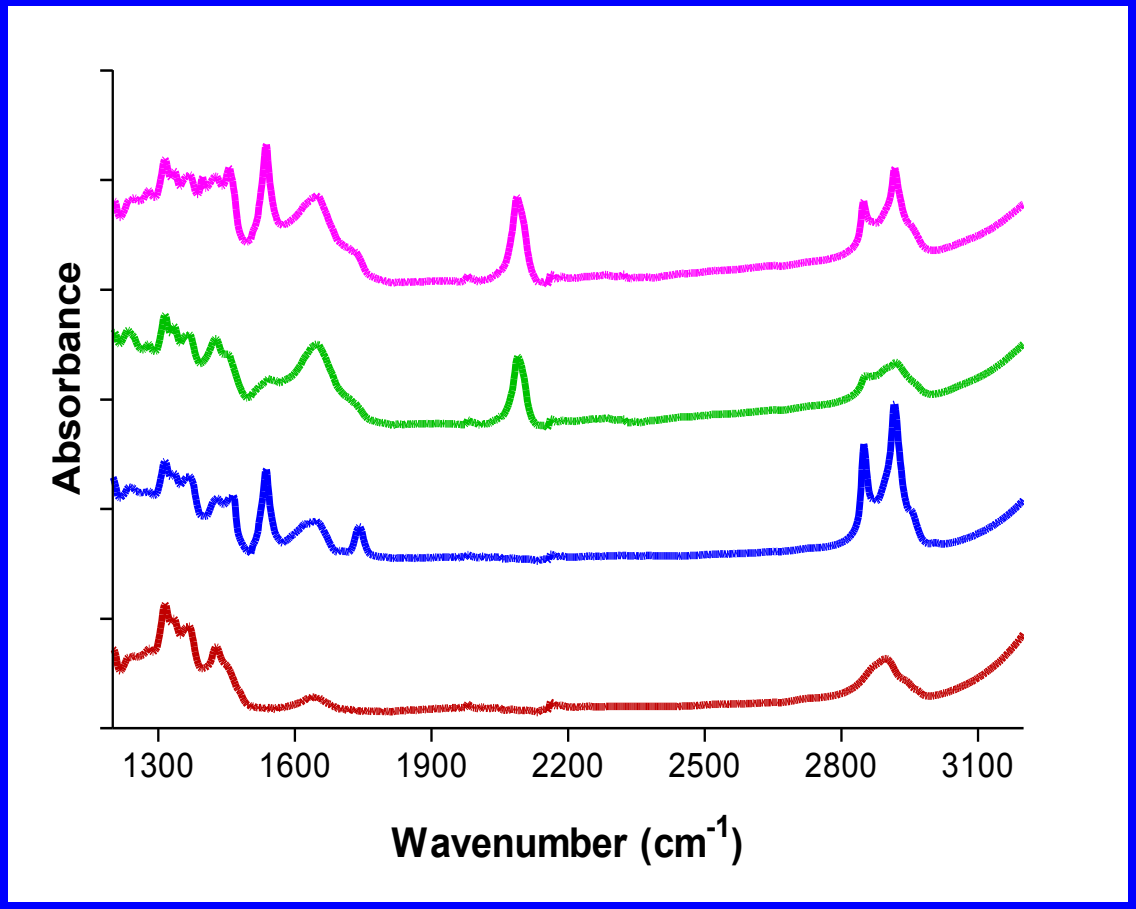
- The printing ink used for the CSA-6 stamps (and for the CSA-7 issues as well) consists of a mixture of Prussian blue (the blue pigment) and talc (the white pigment).
- The actual color of a given stamp will depend on the relative amounts of blue and white pigment used to prepare the ink.
- But the pigment composition of the ink cannot be used to distinguish between London prints and Richmond prints.

IIIa: IR Spectrum of beef fat ground into microcrystalline cellulose



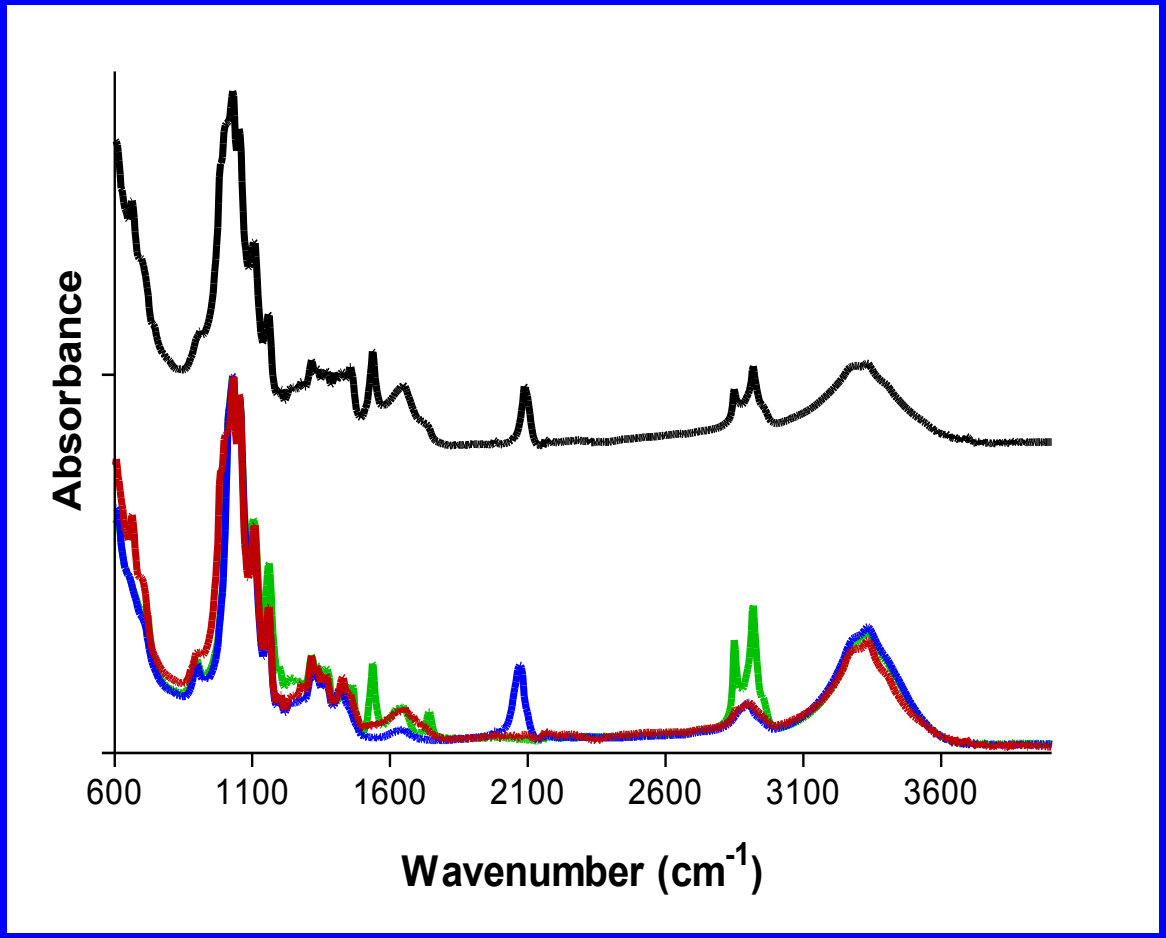
- Magenta trace = CSA-7; Richmond paper
- Green trace = CSA-6
- Blue trace = beef fat in MCC
- Red trace = microcrystalline cellulose

IIIb: IR Spectrum of the MCC - beef fat product exposed to hydrogen peroxide to simulate the oxidation process associated with ink drying



- Magenta trace = CSA-7; Richmond paper
- Green trace = CSA-6
- Blue trace = oxidized beef fat in MCC
- Red trace = microcrystalline cellulose

IR Spectral Analysis of CSA-7



- Black trace = CSA-7R
- Green trace = Oxidized beef fat in microcrystalline cellulose
- Blue trace = Prussian Blue in microcrystalline cellulose
- Red trace = Talc in microcrystalline cellulose

FTIR Study Conclusions (3)

- The printing ink used for the CSA-7 stamps contained a significant amount of oxidized animal fat, and the non-volatile part of this oily fat still remains in the stamps.
- Any oil used in mixing the printing used in the printing of the CSA-6 stamps was much more volatile than the oil used for the Richmond prints, and left very little residual non-volatile component. Most likely, this was a vegetable oil.
- Thus, FTIR spectroscopy can be used to distinguish between London prints and Richmond prints.

Differentiation Summary

- CSA-6 (London ink and London paper)
  - XRD = cellulose paper; no kaolin
  - FTIR = little or no oil residue
- CSA-7L (Richmond ink and London paper)
  - XRD = cellulose paper; no kaolin
  - FTIR = significant level of oxidized fat residue
- CSA-7R (Richmond ink and Richmond paper)
  - XRD = paper contains XRD peaks of kaolin
  - FTIR = significant level of oxidized fat residue

Acknowledgements

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

Any Questions?