Historical Stamp Inks Identification with i-Raman EX®

Introduction:

Stamps are cultural heritage objects that provide an invaluable amount of historical information. As historical stamps can hold a high monetary value as collector's items, there is an increase of counterfeit historical inks. It is imperative that fraudulent stamps can be identified and removed from the market. This case study uses portable Raman to identify the colorants used in stamps on a historical envelope from 1885.

The i-Raman EX® is a portable Raman device with a 1064 nm laser. The i-Raman EX is used in this study to minimize the fluorescence of the ink that is overwhelming with a 785nm laser. The functionality of the low laser power reduction down to 1% prevents sample burning and the Raman video microscope system analyzes small details. These features make the i-Raman EX a useful and nondestructive tool for cultural heritage analysis.

Methodology:

An i-Raman EX with a BAC151 Raman video microscope was used to analyze three areas on a historical envelope (Fig. 1). The samples were placed on the Raman video microscope stage and brought into focus with a 50x microscope objective (Fig. 2a). This objective has a working distance of 3.68 mm and laser beam spot size of 42 µm. The laser power was set between 3%-5% of the maximum laser power (~9.9-16.5 mW) with integration times between 30-60 seconds. Dark scans of equal integration times were taken and subtracted from the measurements. The spectra acquired in BWSpec® software were analyzed by BioRad's KnowItAll software that has a robust spectral library for identification purposes.

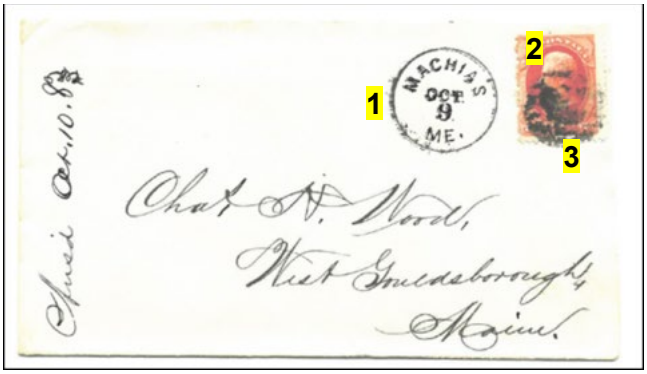


Figure 1. Historical Envelope with three unknown ink areas

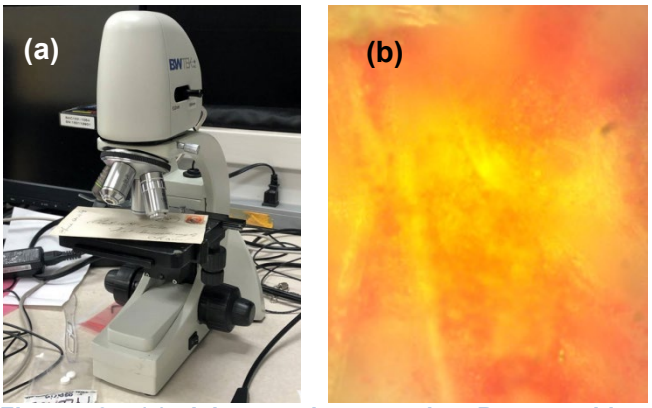


Figure 2. (a) Ink samples on the Raman video microscope stage and (b) image of area 2 red ink at 50x magnification.

Results:

Figure 2b shows the image from sample area 2 taken with the 50x objective. The i-Raman EX with a Raman video microscope system identified distinguishing peaks for the three unknown historical ink samples. Figure 3a shows the Raman spectrum acquired from area 1. The broad peaks at ~1300 cm^{-1} and 1590 cm^{-1} are consistent for the D and G bands respectively of carbon black ink. Spectra acquired from area 3 are also consistent with carbon black ink. Figure 3b shows the spectrum acquired from the ink of area 2. The sharp peaks at 252 cm^{-1} and 344 cm^{-1} are consistent with the Raman signal of vermilion, a bright red pigment made of mineral

containing mercury sulfide. The weak, broad peak at ~838 cm^{-1} is consistent with chrome yellow, a yellow pigment made of lead (II) chromate. The presence of chrome yellow with the red vermilion may account for the slightly more orange hue of the stamp than would expected from only vermilion.

The results were confirmed using BioRad's KnowItAll software. The software calculates a hit quality index (HQI) for each spectrum, representing the correlation of the sample spectrum to a library spectrum. An HQI of 100 is a perfect match. Table 1 shows the software's result of the unknown samples. The spectrum from area 1 matches to carbon black with an HQI of 93.14; the spectrum from area 2 matches vermilion red with an HQI of 97.05 and chrome yellow was identified in a subsequent mixture analysis; the spectrum from area 3 also matches to carbon black with an HQI of 98.29.

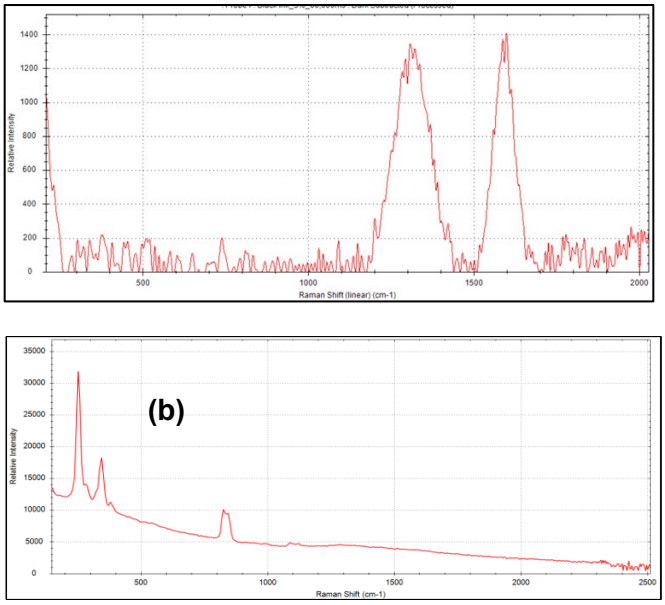
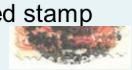


Figure 3. (a) Spectrum collected from area 1 consistent with carbon black (background corrected); (b) Spectrum collected from area 2 consistent with vermilion and chrome yellow.

Table 1. BioRad result of historical ink samples

Sample	BioRad result	HQI
	Carbon black	93.14
	Vermilion (w/ chrome yellow)	97.05
Black ink over red stamp 	Carbon black	98.29

Conclusions:

The i-Raman EX is an effective portable Raman device for the minimization of fluorescence, while maintaining sample integrity of valuable documents. In this case study the i-Raman EX gave distinguishing peaks for inks on an historical envelope. The unknown sample spectra were identified using BioRad's KnowItAll Software.

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