

# Non-Destructive Micro Raman and Micro EDXRF Analysis of the 1d Plate 77 Postage Stamps

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On September 19, 2008, Mr. Abed H. Najjar brought to my laboratory stamps on cover that contained three 1d Plate 77 postage stamps with check letters RL, SK, and SI as shown in Figure 1. The stamps on cover were on an envelope from Guernsey to Brussels. Mr. Robert P. Odenweller arranged the meeting and accompanied Mr. Najjar. In addition, Mr. Odenweller brought 1d stamps from plate 73 and 74 as shown in Figure 2 for comparison of the inks and paper with those stamps on cover. The objectives of the visit was to use non-destructive micro energy dispersive X-ray fluorescence (EDXRF) and micro Raman spectroscopy to determine the elemental and chemical composition of the diamond area surrounding the second “7” in the plate number “77” of the 1d postage stamps.



Figure 1. Annotated Scan of 1865 Guernsey to Brussels Cover Franked With Three 1d Rose-Red Plate 77 Stamps.



Figure 2. Annotated Scan of 1d Plate 73 and 74 Postage Stamps.

## **Analytical Procedures**

### ***Image Analyses***

The analysis of the postal material began by scanning the objects using an Epson scanner. Then, I annotated the scans to produce location maps to illustrate where on the postal materials the analyses was performed as illustrated in Figures 1 and 2. In the figures, “P#” corresponds to the position where the EDXRF beam was positioned to analyze the stamps. These numbers are included as a comment that is embedded in the EDXRF spectrum. Photomicrographs of the second “7” in plate “77” are shown in Figure 3.

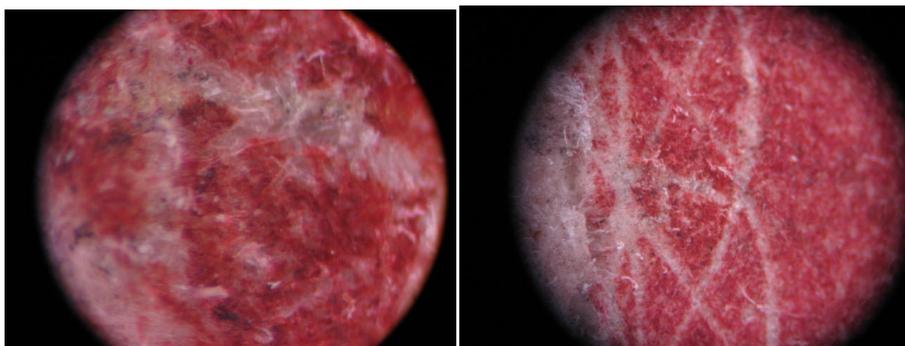


Figure 3. Photomicrographs of second “7”.

### ***EDXRF Analyses***

The second step in the analyses of the stamps was to use micro EDXRF to analyze different locations on the stamps. In EDXRF, an Rh (rhodium X-ray) tube is used to produce

fluorescence X-rays in a sample and only elements determined. With the instrument configured with an Rh tube, only the elements Na (sodium) to U (uranium) can be determined. The X-ray spectrum produced provides both qualitative and quantitative information on the elements in a sample. It is customary to only label the K-alpha (for example CaK) and L-alpha (for example BaL) X-ray peaks in a spectrum (See Figure 4.) and this can lead to confusion for the non XRF spectroscopist to interpret the spectrum and conclude that there are “unknown” or “unlabeled” elements in the sample.

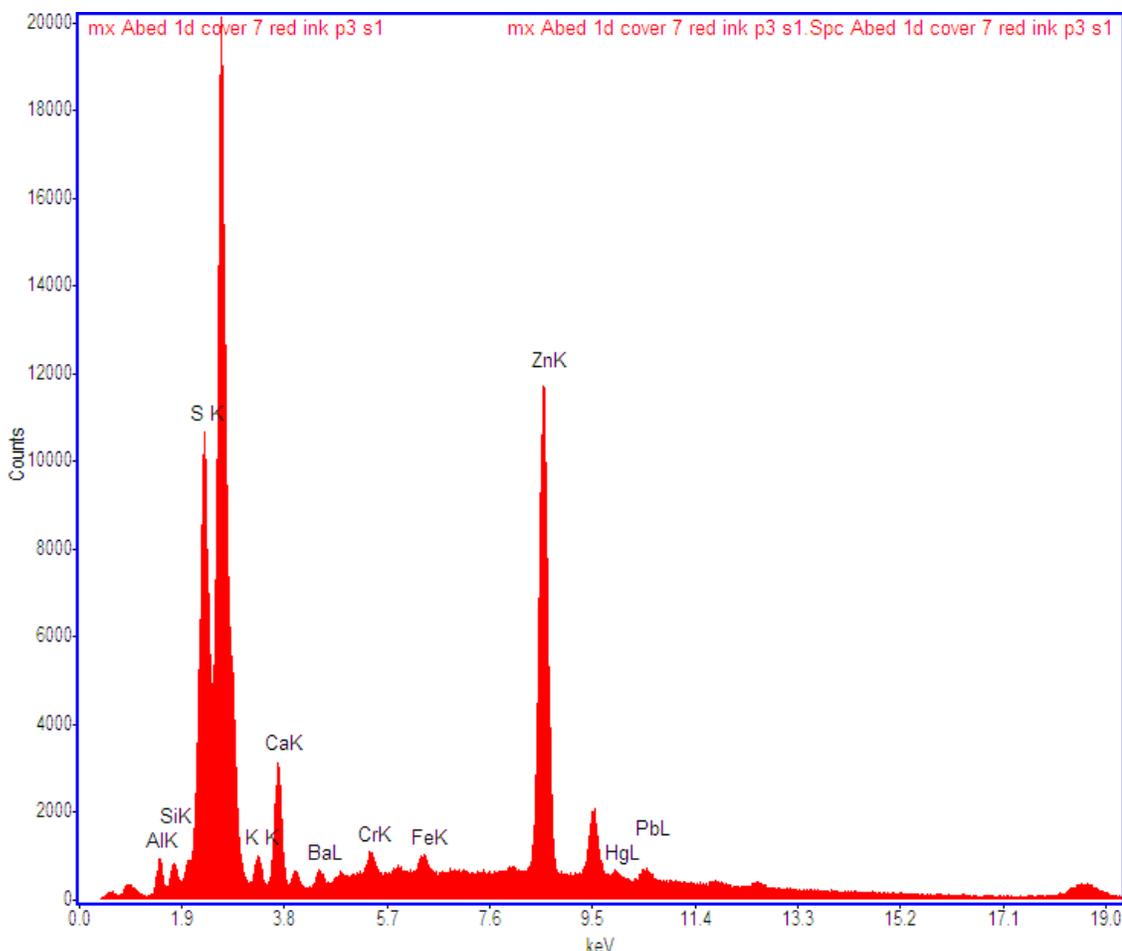


Figure 4. Typical EDXRF spectrum showing only the K and L lines.

The strategy of the EDXRF analyses was to analyze the diamond inked area around the second “7” in the plate number “77”. The X-ray spectra from this area were compared to that collected from the area surrounding the first “7” in the plate number “77”. In addition, I also analyzed stamps from plate 73 that included areas around the “3” and “7” in plate number “73”.

Briefly, I used an EDAX International (Mahwah, NJ) micro EDXRF Eagle II spectrometer to analyze the stamps. The instrument has an Rh X-ray tube attached to a polycapillary lens to focus the Rh X-rays to spot size of 40-microns. The sample is mounted onto a computer controlled x, y, z stage to position the stamps so that specific features (ink,

paper, cancelation marks, metal fragments) of the stamp can be analyzed. Typical analyses conditions of the locations on the stamps used 35-kV operating tube voltage with a current of 200 micro amps. Typical analyses times per spot were 400 seconds. The individual locations from where the analyses were performed were saved to the hard disc with the peaks labeled corresponding to the elements found at that location.

EDXRF revealed that elements in the red-rose ink around the first “7” in the plate number on stamps from 1d Plate 73 and 77 contained Hg (mercury), S (sulfur), and Pb (lead). The high concentration of Zn (zinc) is due to ZnO, a white pigment that is in the paper from the envelope. Other elements such as Al (aluminum), Si (silicon), Ca (calcium), and K (potassium) are due to fillers in the stamp paper. Iron (Fe) is perhaps due to trace impurities in the water used to make the paper pulp. Although the intensities (peak heights) of the various elements in the EDXRF spectra varied from location to location, this does not mean the composition of the ink was different. Because the analysis was performed with an X-ray beam spot size of 40-microns, variations in ink coverage on this micro scale will show differences because the spreading of the ink is not homogenous on this micro scale.

EDXRF also revealed that the diamond inked area around the second “7” in plate number “77” contained the same elements (Hg, S, Pb, Ca, K, Al, Si) as in the diamond inked area around the first “7” with additional elements of Ba (barium), Cr (chromium), and P (phosphorous) in a spot location and was not homogenously distributed around this diamond inked area. The elements Ba, P, and Cr were not found in the diamond area around the first “7” in the plate numbers “77” and “73”. The EDXRF spectra summarizing this finding are shown in Figure 5.

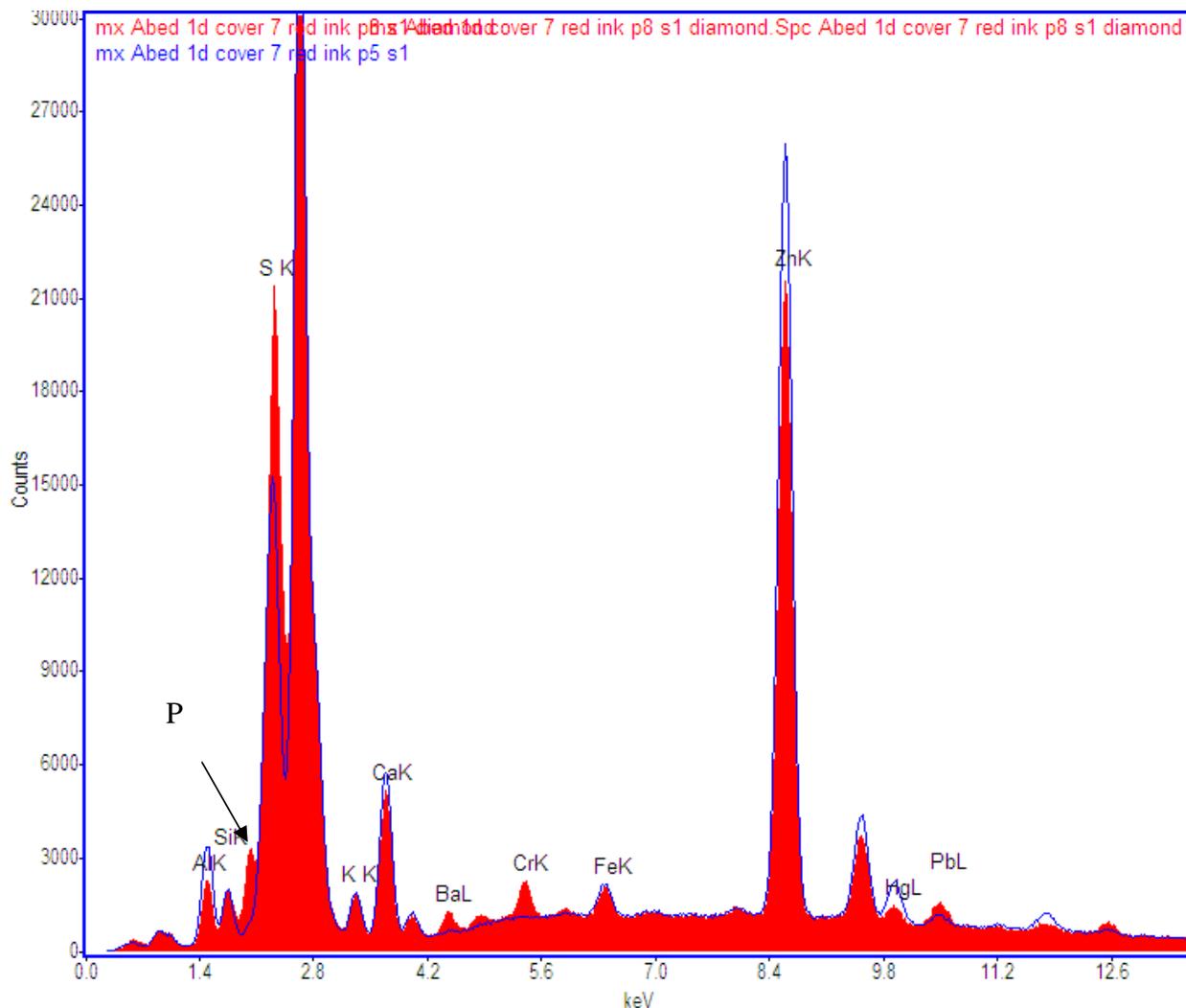


Figure 5. EDXRF comparison of red ink around first (blue trace) “7” and around second (red trace) “7” in the plate number “77”. Notice the appearance of P, Ba and Cr in the second “7”.

### ***Micro Raman Analyses***

For the third analyses, I used micro Raman spectroscopy to determine the chemical composition of the ink and paper from which the EDXRF revealed elemental compositions. Raman and EDXRF are complementary analytical techniques in that EDXRF determines the elements and Raman can determine the chemical compound that these elements belong to. This is only possible if the chemical compound is in a reasonable concentration and the compound is a high Raman scatterer.

A Renishaw (Hoffman Estates, IL) system 1000 Raman microscope equipped with a Leica microscope was used to analyze the chemical composition of the pigments in the printing inks used on the stamps. Raman scattering in the stamps were produced by excitation with 785 nm diode laser. The beam size of the laser was 2 microns, using 50x objective lens, and the laser

power at the sample surface was reduced to 15 mW to prevent any damage due to burning of the stamps. Figure 1 shows the location of the analyses. Emphasis was focused on areas around the second “7” diamond area (See Figure 3) that showed the presence of additional elements of P, Ba, and Cr from the EDXRF analyses.

Raman analyses revealed that the red pigment on the stamps are composed of HgS (vermillion) and red lead ( $\text{Pb}_2\text{O}_3$ ). Unfortunately, the chemical compound associated with Ba that was determined by EDXRF could not be identified. It is assumed that it is  $\text{BaSO}_4$  (barium sulfate or barite).

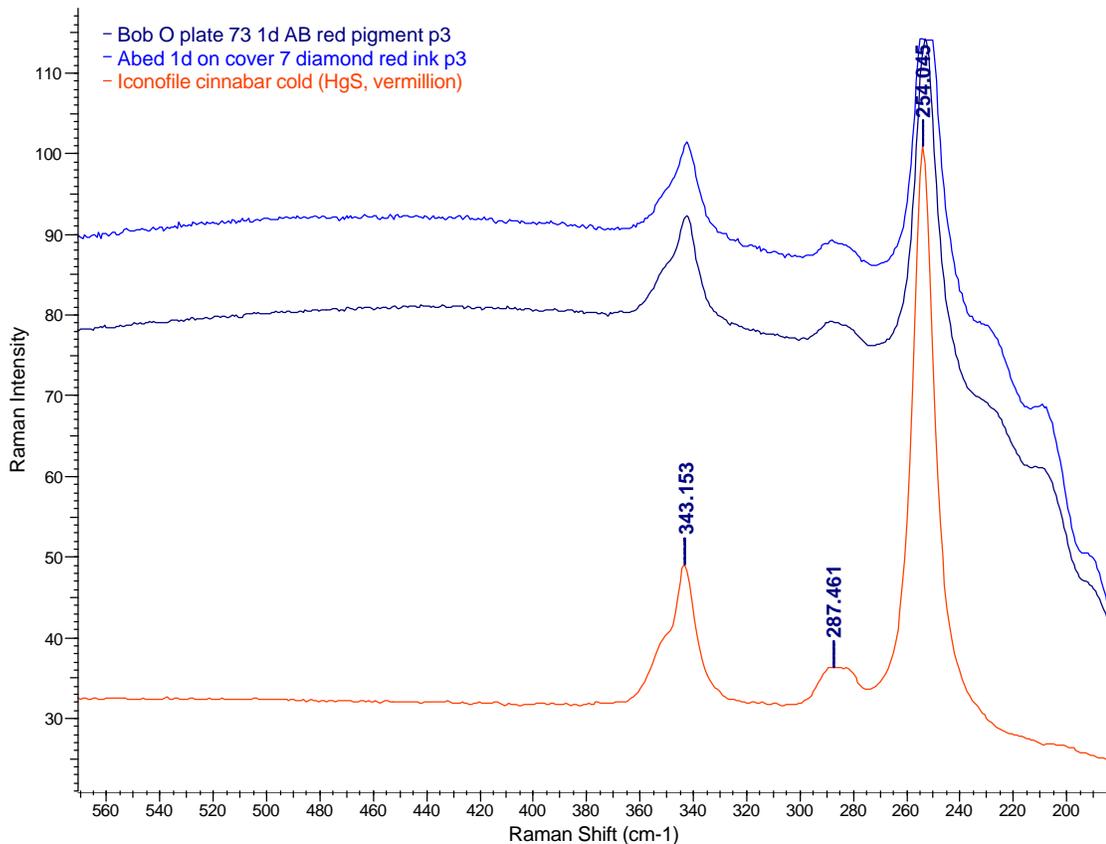


Figure 6. Raman spectra comparison of red ink on the diamond area around the second “7” and “3” in plate numbers “77” and “73”.

In addition, analyses of the inked area around the second “7” in plate number “77” contained the same ink composition ( $\text{HgS}$ ,  $\text{Pb}_2\text{O}_3$ ) that are in the diamond area around the first “7” with the addition of microscopic particles that contained  $\text{PbCrO}_4$  as shown in Figure 7.

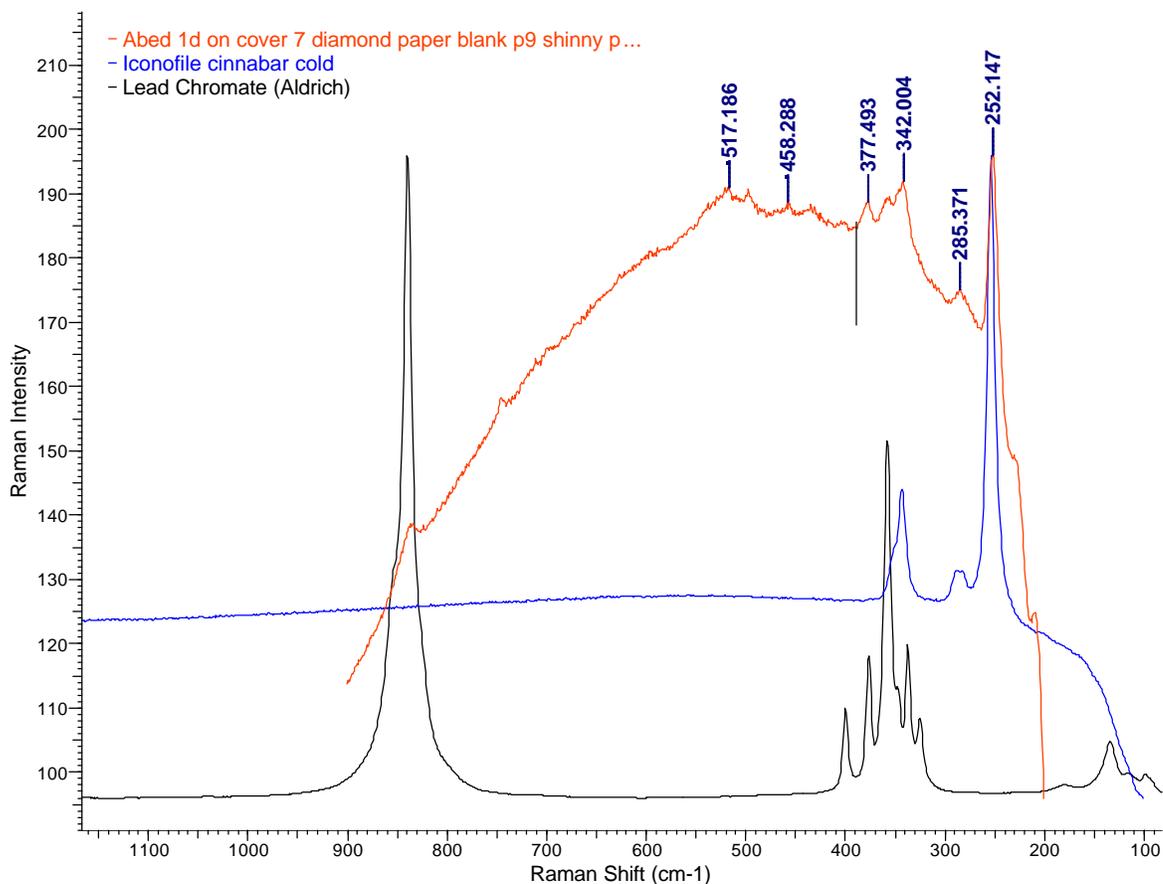


Figure 7. Raman spectra comparison diamond area around second “7” in plate “77”

## Conclusions

Two complementary micro analytical techniques of Raman spectroscopy and EDXRF were used to analyze the elemental and chemical composition of the 1d Plate 77 and 73 postage stamps. The red ink on the stamps is composed of HgS (vermillion) and Pb<sub>2</sub>O<sub>3</sub> (red lead). There was no difference in the ink composition in the diamond areas surrounding the first and second “7” in the plate numbers. The elements Ba, Cr, and P were found only in the diamond area surrounding the second “7” in plate number “77” and were not homogenous and not part of the ink formulation. Their source is probably from the printing process. Barium, P, and Cr were not found in the red ink surrounding the first “7” in plate number “77”. The Cr was due to the chemical compound PbCrO<sub>4</sub> (chrome yellow) and was confirmed using the complementary technique of Raman spectroscopy.

The complementary techniques of micro Raman spectroscopy and micro EDXRF are excellent non-destructive analytical techniques for determining the elemental and chemical composition of postage stamps. This information can assist in the authenticity of the postage stamps.

### **Future Tasks and Recommendations**

It would be very useful if other 1d plate 77 stamps could be analyzed by both Raman and EDXRF to see if  $\text{BaSO}_4$  and  $\text{PbCrO}_4$  are present in the diamond area surrounding the second “7” in plate “77”. In addition, I recommend using SEM to scan around the second “7” to determine the size of the particles containing  $\text{PbCrO}_4$ . For a second analyses using EDXRF at my laboratory, I would do elemental image analysis around the second “7” to generate elemental maps showing the distribution of the elements. Maps can determine if there is an elemental image showing particles or alphanumeric characters. This was not done when the stamps were first brought to my laboratory because of time constraints. A typical elemental image analysis on one location would take approximately 3 hours. Finally, the source of the  $\text{PbCrO}_4$  in the stamps has to be determined. This would perhaps help determine how plate 77 was used to print the stamps. It should be noted that  $\text{PbCrO}_4$  is a yellow pigment that is used in printing inks and  $\text{BaSO}_4$  is used as an extender pigment.