

Metals in Paper and Ink of “U.S. Three-Cent Bank Note Stamp”

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Abstract

More than 6.6 billion of “United States three-cent banknote” stamps were printed during 1870-1881. They were printed in three different companies, National B.N.C., Continental B.N.C., and American B.N.C., which was using two differently engraved image carriers. Color variation in inks of all these stamps was examined via non-destructive qualitative fluorescent spectroscopy, using EAGLE III μ Probe – Energy-dispersive X-ray Fluorescence Spectrometer. It was found that ink in stamps contained calcium, barium, lead, zinc, iron, chromium, silica and aluminum. Relative levels of the metals in the inks varied, which probably resulted in color variation between those stamps. Stamps from 1878 and newer did not contain zinc in inks. Also, the relative level of metals in individual series of stamps varied, namely in levels of Ca, Ba, Pb, and Zn. Non-printed areas of those stamps were also analyzed for metals content. It reveals that every company used paper with different metals: in National paper was found Ca, in Continental Ba and Zn, in American – Ca, and in American re-engraved paper Cu, Fe, Mn, Mg, Si and Al were found. This indicates that each company was using different paper, which could lead to color variation between stamps originating from different companies.

Introduction

Early inks used for printing stamps in 19th –early 20th century contained elements such as sulfur, lead, iron, potassium, calcium, lead, mercury, aluminum, chromium

and barium. These elements were components of various inorganic salts like Cr_2O_3 and PbCrO_4 , making up green pigments, $\text{Pb}(\text{OH})_2$ and Pb_3O_4 inorganic orange pigments, HgS (cinnabar) and hematite, Fe_2O_3 , being components of red pigments. Prussian blue ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$) is likely component of blue ink compositions for stamps printing [Castro et al, 2008]. A combination of Prussian blue, a synthetic iron (III) hexacyanoferrate (II) pigment ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 14\text{--}16 \text{ H}_2\text{O}$) and chrome yellow (PbCrO_4) was used for green inks. As an example, this pigment combination was found on 1858–62 early Mauritius green Britannia-type postage stamps. When the stamp was printed with premixed Prussian blue and chrome yellow, the ink pigment was called “chrome green”, while forged green stamps were sometimes made by coating blue stamp with solution of chrome yellow. Baryte (BaSO_4) and calcium carbonate (CaCO_3) served as white extender for pigments, carbon black (C) was found to be pigment used in cancellation inks.

Ultramarine blue, a sodium aluminosilicate mineral ($\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{Sn}$) was sometimes found in between pulp fibers of the stamps, most likely with the aim to enhance the brightness of the paper of the stamp, as found in forgeries of Mauritius stamps [Chaplin, 2004]. Some inorganic compounds were added to ink formulations for security reasons. A good example is potassium prussiate or potassium hexacyanoferrate ($\text{K}_4\{\text{Fe}(\text{CN})_6\} \cdot 3\text{H}_2\text{O}$), which was found during analysis of one-penny stamps printed in Britain in 19th century [Ferrer, 2006]. This chemical used to be added to ink to make it more difficult to erase cancellation marks on stamp with the aim of reuse. Fraudulent removal of cancellation marks used to be done with alkaline solutions, which as a side effect caused destruction of images by decomposing potassium hexacyanoferrate [West Fitzhugh, 1997], resulting in a bluing effect of the postal stamps [Ferrer, 2006].

Scientific analyses of stamps in the 20th century was highly underrepresented, and very few stamps were analytically studied in the past [Castro, 2008; Odenweller, 2009; Sanchez, 2006; Jones, 2001; Jones 2002; Ferrer, 2006]. Chemical analysis of stamps was carried out on minimum level, even in countries like UK, France, or Germany [Jones, 2002; Jones 2001]. A spatially resolved x-ray fluorescence (XRF) technique was applied to philately [Sanchez, 2006] to specify elements used in printing inks, which helped in authentication of stamps by revealing fakes. Another spectroscopic method, Fourier transform infrared spectroscopy (FTIR) was applied to the characterization of red inks

used to print one-penny stamps in Britain from the 19th century [Ferrer, 2006], which helped to analyze the development of red ink formulation over period of years 1841-1880. Elemental analysis of ink in stamps was performed by Odenweller [Odenweller, 2009]. The Royal Philatelic Society of London has been publishing results on stamp analyses [Pearson, 2006]. Pigments in inks were analyzed by Raman microscopy [Chaplin et al, 2004], and energy dispersive X-Ray fluorescence [Liston, 2011]. It is clear that this field of analytical philately is highly underdeveloped,

and therefore it is necessary to conduct analytical research in the field inks and papers used in postal stamps production.

More than 6.6 billion of United States three-cent stamps were printed during years 1870 - 1883. Obviously, these stamps were printed on different paper stock, using diverse printing plates, ink colors and most likely various chemistries, and were printed on different printing presses [Barwis, 2001]. The aim of this work was to analyze metals found in paper of the stamps, figure out what caused color differences in print of these stamps. Another goal was to determine if they were printed with the same type of ink, or if several different types of ink were involved.



Figure 1: US Three-cent bank note (not in scale)

Experimental

Stamps for Ink Analysis

Totally, 402 stamps were used for paper and ink analyses [Pekarovic, 2011(A), Pekarovic, 2011 (B)]. The colors are as described in the Scott Specialized Catalogue of United States Postage Stamps. All stamps were soaked in distilled water to remove gum and hinge remnants. They were then air dried, all in a uniform manner. Issue and amount of stamps from individual categories for ink analysis are listed in the Table 1.

Issue	Printer	Stamps
1870	National B.N. Co.	9
1873	Continental B.N. Co.	14
1878	American B.N. Co.	9
1881	American B.N. Co., re-engraved	11

Table 1: Stamps for Ink Analysis

Metals in the ink were measured using an EAGLE III μ Probe – Energy-dispersive X-ray Fluorescence Spectrometer. All the measurements were done in vacuum. The detector was cooled using liquid nitrogen (MCT Cooled). Aperture: 150 μ m x 150 μ m, Signal filter: Beer-Norton. Conditions of the measurements are as follows: Anode: Rh (Rhodium) High voltage: 10-40kV; Current: 20-1000 μ A, Diameter of

X-ray beam: 300-1000 μm (monocapillary). Time of measurement was 100s. Detector: semiconductor Si (Li) with active area 30 sqmm. System Resolution for 5.9 eV Manganese Ka X-rays (Taken with a radioactive Fe55 source): 132.7 eV F.W.H.M. at 1 KCPS, Amplifier Resolution Time: 17 μs . Mechanism of X-ray fluorescence is illustrated on the **Figure 1** and **2**.

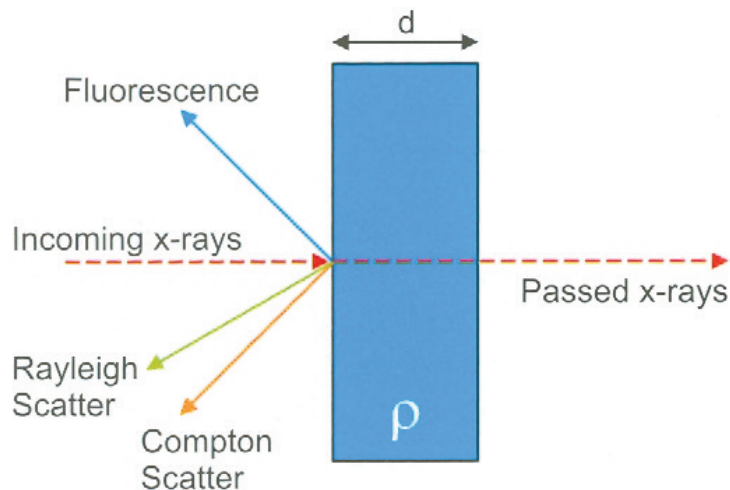


Figure 2: Mechanism of interaction of X-rays with material

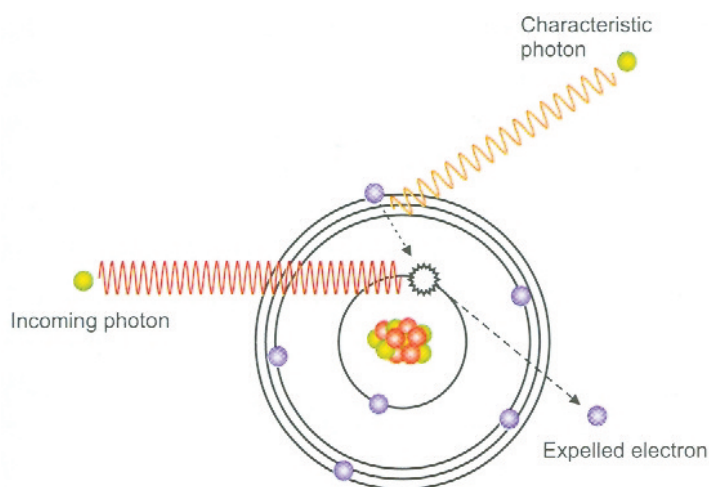


Figure 3: Characteristic fluorescent radiation

IR Spectra

IR spectra were measured on the paper using a Thermo Scientific Nicolet iN10 MX - Fourier Transform Infrared Spectrometer equipped with MCT/A detector, KBr Beam Splitter. The conditions of measurements are given below.

Sample spacing: 2.0000. Number of sample scans: 128; Collection length: 24.7 sec; Resolution: 8.000; Levels of zero filling: 0 Number of scan points: 4384;

Number of FFT points: 4096; Laser frequency: 15798.0 cm⁻¹ Interferogram peak position: 2048; Apodization: N-B Strong; Phase correction: Mertz ; Number of background scans: 128; Background gain: 1.0

DATA DESCRIPTION- Number of points: 863; X-axis: Wave numbers (cm⁻¹); Y-axis: Absorbance; First X value: 674.9634; Last X value: 3999.6401; Data spacing: 3.856934; Digitizer bits: 24; Optical velocity: 2.5317; Aperture: Medium resolution; Sample gain: 1.0; High pass filter: 200.0000; Low pass filter: 20000.0000.

Results and Discussion

Totally, 402 stamps were used for analysis. Metals were analyzed using an EAGLE III μ Probe – Energy-dispersive X-ray Fluorescence Spectrometer. Analyses were done on printed and non-printed areas of stamps. X-rays interact with matter resulting in fluorescent, radiation, Compton scattering and Raileigh scattering [Brouwer, 2003]. If X-rays fall onto the surface of the material, some rays get transmitted, others are absorbed and generate fluorescent radiation, and the rest is scattered away. Fluorescent radiation is dependent on composition of the material, its thickness and density [Brouwer, 2003] of irradiated material. X-ray irradiation may expel electron from metal atom, namely from its shells or orbitals, such as K, L, M shells. X-ray energy has to have higher energy than binding energy of the electron. If the atom is expelled, the radiation is absorbed. Fluorescence depends on the energy - the higher the absorption, the higher is the fluorescence. However, there are certain rules which apply pertaining fluorescence yield from electrons originating from different shells [Brouwer, 2003]. The example of the obtained fluorescent spectrum of metals originating from K,L,M shells is illustrated on the Figure 4. The elements found in the inks were calcium, barium, lead, zinc, iron, chromium, silica, and aluminum (Table 1).

Medieval documents were analyzed for metals in inks and paints by Raman microscopy [Clark, 1995]. Clark found origin of various pigments used in written and printed documents from 13- 19 century. Calcium may come from calcium carbonate or sulfate [Clark, 1995], used as ink filler or extender. Barium may be portion of barium sulfate, very insoluble mineral, which was used in inks as white extender [Oliayiy, 2009], or barium yellow, chemically barium chromate BaCrO₄. Chromium in green inks used to be partially Cr₂O₃. 2H₂O, viridian, and PbCrO₄, chrome yellow. Chrome yellow is a natural pigment made of lead(II) chromate, usually coming from mineral crocoite. Viridian is a dark green pigment [Buxbaum, 2008; Clark, 1995] of hydrated chromium (III) oxide (Cr₂O₃). Light green pigment consisting of a mixture of Chromium sulphide (CrS) and Viridian (Cr₂O₃), may be also inorganic green pigments used in these inks. The lead is one of the metals responsible for green color in these inks. Lead chromates form a spectrum of yellows with green shades, and use to be extended with alumina hydroxide [Leach, 2007].

Iron can be present in inks as naturally occurring yellow ochre, clay of hydrated iron (III) oxide ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$). Ochres are among the earliest pigments used by mankind. These clays contain also various mineral oxides. Zinc may come from mineral Spinel $\text{Fe}_2\text{O}_3 \cdot \text{ZnO}$, or zinc ferrite, inorganic pigment yellow [Buxbaum, 2008]. Possible origin of zinc may be from zinc silicates, which could be used as fillers and/or extenders, and that also justifies the presence of silica in inks [Krysztalkiewicz, 2001]. Zinc may be a component of white pigment “lithophone”, mixture of zinc sulfide and barium sulfate, or simply zinc oxide ZnO [Clark, 1995]. Silica and aluminum may come from “green earth”, hydrous aluminosilicate of iron [Clark, 1995].

A summary table for metals found in three cent stamps from 1870-1881 (Table 1) shows, that the metal composition of inks was fairly similar; however, there are some differences, mainly in zinc, barium, calcium, and lead level in the inks. Highest amounts of barium were found in “Dark green” of 1870 and 1878 editions, and green of 1878 edition. (Table 1). Barium was not found in 1873 Green, and 1873 Dark green, the rest of stamps had similar low level of barium in their inks. American and American re-engraved differ from the rest of older stamps by completely missing zinc in their inks. Far highest zinc level was found in “Dark green” 1870. Overall, 1870 Edition was richest in zinc than the rest of stamps, followed by 1873 Edition, which had higher level of zinc in “Yellow green” and “Olive green” (Table 1). Concerning calcium, highest level of it was found in 1881 “American” re-engraved, blue green stamps, followed by “Yellow green” 1881, “Dark green” 1878 and “Yellow green” 1873, which may indicate that calcium was used as extender to change hue of inks. Highest amount of lead was found in “Green” stamps 1873 edition, followed by dark green 1870, dark green 1873, olive green 1873 and green 1878. Lesser amount of lead was found in the rest of the stamps, but all of them had lead in their inks. There were no high levels of chromium found in inks, slightly higher levels were found in 1870 Dark green and 1873 Olive green, the rest of stamps had similar level of chromium (Table 1). There is fairly similar level of iron in all inks except 1878 “Green”, which contains slightly higher level of iron (Table 1). Inks, used for printing National BN contain the same group of metals (Ca, Ba, Pb, Zn, Fe, Cr, Si and Al), which shows that the chemistry of inks used by National BN Co was identical for all stamps, color difference may come from non-consistent ink deposition for 1870 issue of stamps, but also from paper differences, which were also confirmed [Pekarovic, 2011A]. Silica and aluminum are almost in all cases present in the same levels (except 1873 Yellow green and 1881 blue green) or completely missing 1873 green, dark green, and olive green. Actually, only 1873 Edition is missing aluminum and silica in their inks (Table 1). Overall, some of Continental stamps have ink containing the same metals as National BN (Ca, Ba, Pb, Zn, Fe, Cr, Si and Al), but “Green”, “Dark green” and “Olive green” are lacking Si and Al, and “Green” and “Dark green” are also lacking barium.

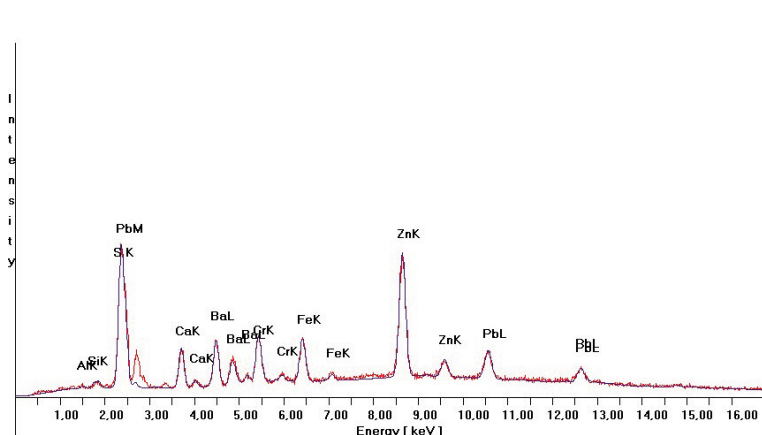


Figure 4: Energy-dispersive X-ray fluorescence spectrum of ink of olive green 1873 stamp

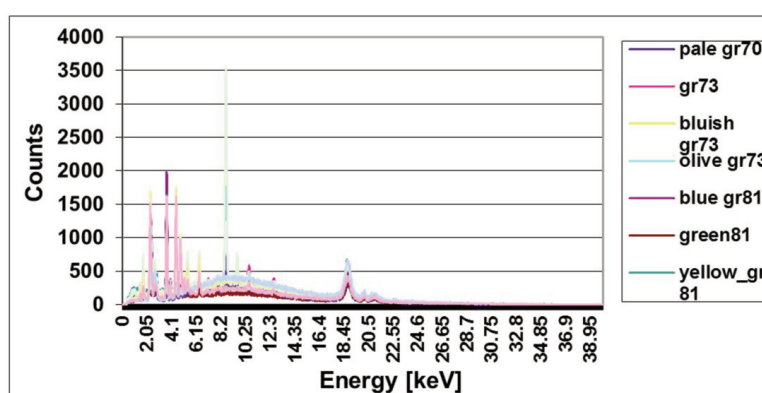


Figure 5: Energy dispersive X-ray fluorescence spectra of all inks

Issue	Stamp color	Metals in the ink							
		Ca	Ba	Pb	Zn	Fe	Cr	Si	Al
1870	Green	x	x	x	x	x	x	x	x
1870	Pale green	x	x	x	x	x	x	x	x
1870	Dark green	x	x	x	x	x	x	x	x
1873	Green	x		x	x	x	x		
1873	Bluish green	x	x	x		x	x	x	x
1873	Yellow green	x	x	x	x	x	x	x	x
1873	Dark green	x		x	x	x	x		
1873	Olive green	x	x	x	x	x	x		
1878	Green	x	x	x		x	x	x	x
1878	Light green	x	x	x		x	x	x	x
1878	Dark green	x	x	x		x	x	x	x
1881	Green	x	x	x		x	x	x	x
1881	Yellow green	x	x	x		x	x	x	x
1881	Blue green	x	x	x		x	x	x	x

Table 2: Metals in inks of “United States Three-Cent Bank Note” stamps

Issue	Stamp color	Metals in the paper								
		Ca	Ba	Cu	Zn	Fe	Mn	Mg	Si	Al
1870	Green	x								
1870	Pale green	x								
1870	Dark green	x								
1873	Green		x							
1873	Bluish green									
1873	Yellow green				x					
1873	Dark green									
1873	Olive green				x					
1879	Green	x								
1879	Light green	x								
1879	Dark green	x								
1881	Green			x		x	x	x	x	x
1881	Yellow green								x	x
1881	Blue green			x		x		x	x	x

Table 3: Metals found in the stamp paper

Conclusion

Our work done by Energy-dispersive X-ray Fluorescence Spectrometry confirmed that ink in stamps contained metals such as calcium, barium, lead, zinc, iron, chromium, silica and aluminum. Relative levels of the metals in the inks varied within companies, which probably resulted in color variation between stamps. Stamps from 1878 and newer did not contain any zinc in inks. Level of metals in individual series of stamps varied, namely in Ca, Ba, Pb, and Zn levels. Metals found in paper: National BN. Co paper - Ca, Continental BN Co. - Ba, Zn, American – Ca, and American BN Co. re-engraved: Cu, Fe, Mn, Mg, and Si. Thus, each company was probably using different paper, which could also cause color variation. The fact that each company was using different type of paper was confirmed sooner by bending indices analysis, and fiber analysis in Part I of this project [Pekarovic, 2011].

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