Synopsis

A Spectroscopic Study of Three Issues Cataloged as Blue Colour Errors

Purpose and Scope: I have limited this exhibit to three examples where spectroscopy is used to 1) confirm a catalog pigment error 2) to explain and narrow a catalog pigment error and 3) to correct a catalog pigment error.

Importance: Catalogue listings are the primary source for most stamp collectors and are of significant importance for philatelists. This exhibit will show the unequivocal value of spectroscopic instruments in either confirming, limiting the criteria as an error or correcting these listings.

Treatment: I have attempted to keep the scientific jargon to a minimum. The graphical representations shown in the exhibit are designed to show either the *differences* or *lack thereof* between the common and the error. This is illustrated by the choice of three examples.

The US Columbian 4c Prussian Blue Error: A well known and expensive error that is correctly identified. Here, the infrared spectrum (FTIR) shows the error contains the Prussian blue pigment while the normal does not. Plate proofs and regular issues of the 1c and 4c are displayed beside the error. The source of the error is the use of the pigment from the 1c issue.

Newfoundland 'Trail of the Caribou' Prussian Blue Error: The error and the normal stamp have nearly identical ink chemistry supported by FTIR and X-Ray Fluorescence (XRF). All contain Prussian blue. The study had 34 regular issue stamps and 3 expertized copies. Only the RPL copy is in the exhibit, and 12 other copies were returned to their owners. (See addendum)

United Nations First Airmail Issue Prussian Blue Error: The previous two sections set the stage for this last and most important study. The earlier sections attest to the scientific method as applied here. Two certified UN Prussian blue copies contain the Prussian Blue pigment. But so do the other 97% of the approximately150 stamps studied. A remaining 3% contain NO Prussian blue pigment and further contain additional elements (chromium and lead). The reflectance spectrum in the near IR of the 3% is radically different than the majority. It is the contention here, the catalog, although correctly identifying an error, had done so for the wrong reason. The aim of the exhibit is to guide the viewer though the spectra provided to come to the conclusion that the reliance on human vision as the sole determination of shade errors can and does lead to errors.

Research: The source of the Columbian 4c error has been well documented before (see reference list) and was included in the exhibit to give a clear example of an accepted error. The Newfoundland error study was initiated by Garfield Portch and John Walsh. They supplied certified copies (Greene Foundation and APS) and I supplied a RPSL copy. Amongst the three of us (and from other sources) , 34 copies of uncertified copies were added to the study. As the exhibit shows, all copies show similar ink chemistry. The scientific literature confirms that small

shade differences will appear depending on the method of preparation of the pigment and the particle size (see addendum). The UN study came about by a chance when checking the catalog value of the 15c first airmail issue and I noted a Prussian Blue error existed. Two certified copies were purchased : PF (2012) plate block of 4 and a Gordon (2012)/ APS (2020) single. These were found to be identical to the normal copies on hand, all with Prussian Blue but in varying amounts. As this is an inexpensive stamp, easily obtained, additional stamps were purchased. It was with excitement, that I found a single stamp that had no Prussian Blue. This spurred additional purchases and with approximately 150 stamps and covers, a total of four singles and one pane are found to be the error that is described in the literature (see references). Thirty covers with clear data stamps have been purchased in the hope of finding the error on cover and thus fixing the data of the error but has not been successful to date.

Condition and Rarity: A reasonably centred copy of the Columbian Error is shown. It is considered a major and scarce error. The Newfoundland Trial of the Caribou certified copies of the error can be found with some searching and purchased at about 8x the normal copy. One copy from RPSL is shown. The UN error is offered occasionally through Ebay at about 100 times the normal copy for a certified copy ($60), now shown to be incorrectly identified as an error. Two copies are shown. Since 3% of the UN issue are identified as true errors in this study, then the full sheet displayed in the exhibit is likely scarce.

Relevant Literature:

FTIR Methods**:** Harry Brittain, " Use of X-Ray Diffraction and Infrared Absorption Spectroscopy for the Study of Paper and Ink in Postage Stamps". Proceedings of the Fourth International Symposium on Analytical Methods in Philately Edited by Thomas Lera and John H. Barwis. 2020 pp 1. (See PowerPoint Presentation on FTIR near the middle)
https://drive.google.com/file/d/10TIzB5goE3gZVuWT3tv3n9B4X8YpqTaC/view
XRF and FTIR Methods: Chown, Steve, Thomas Lera and Charles Neyhart "Regulatory ink change and an unrecognized color variety: the 25c Frederick Douglass definitive", The United States Specialist 85 (11) 1017 (2014) pp 501- 512.
Columbian Prussian Blue 4c (233a): Lera, Thomas "Determination of the Pigment Used in the 1893 4 Cent Columbian Color Error (Scott 233a)", Collectors Club Philatelist 93(3) 2014 pp 153-160.
Newfoundland Prussian Blue: Walsh, John M. "Newfoundland : 1919 Caribou Issue 15¢ Denomination. Its True Ink Ingredient Structure Discovery" Maple Leaves 36 pp. 461-471 2020
UN First AirMail: Kvarnes, Robert G. "The First Issue of United Nations postage stamps, 1951-1966", Self Published 198? , APRL Call Number: HE6239 .U5 K97f. Relevant pages 11 and 19-20.
Prussian Blue Pigment: Samain, Louise et al, 'Relationship between the Synthesis of Prussian Blue Pigments, their Colour, Physical Properties and Their Behaviour in Paint Layers'; J. Phys. Chemistry C117, 2013, pp 9693 – 9712

Relevant Research Articles by the Exhibitor:

R.H. Judge "Philatelic Applications of Wavelength Resolved Fluorescence", Proceedings of the Fourth International Symposium on Analytical Methods in Philately Edited by Thomas Lera and John H. Barwis. 2020 pp 71-78
R.H. Judge "Chemistry of Aniline inks, 2-cent Admiral Issues of Canada". Proceedings of the Third International Symposium on Analytical Methods in Philately." Edited by Susan Smith and John H. Barwis, 2017, pp 11-24
R.H. Judge "The Admiral Issue of Canada: A Colorimetric and XRF Study of the Carmine 2¢ Issue." Proceedings of the Second International Symposium on Analytical Methods in Philately Edited by John Barwis and Thomas Lera 2015, pp 21-30
Portch, Garfield, John M. Walsh and Richard H. Judge. "Does a 'Prussian Blue' Shade Variety Exist for the 15c Newfoundland 1919 Trail of the Caribou Issue? " The Newfoundland Newsletter, 178 (2020) pp 7-10.

Addendum:

As an aid in interpreting the spectra shown here, additional information about the science behind the exhibit is presented.

The XRF spectra will capture the elements present in the whole stamp, ink, paper and gum plus any impurities within the paper. Also some background from the instrument is present and accounts for weak iron, nickle and copper peaks present in all spectra. This XRF instrument will not be able to observe elements lower than sodium and thus organic compounds like cellulose (paper) will not be seen.

The FTIR will be able to identify molecular and ionic compounds in the ink. Because the sampling area is small and since the infrared beam from this type of FTIR only penetrates microns into the surface of the stamp, potentially only the ink can be studied. However, with engraved stamp, ink free areas are present and thus the paper may also be seen in lightly engraved areas. These extra peaks due to paper are easily identified as microcrystaline cellulose. However, they do obscure the peaks from other compounds. FTIR is often called a fingerprinting technique. Absorption peaks from pure chemical compounds have nearly unique patterns. If this pattern is seen in the FTIR spectrum of a mixture, it is considered proof of its presence. This is the case for Prussian blue with a series of sharp peaks where one is due to the cyanide group (CN) that sits alone at ~2100 cm^{-1}. Other compounds identified in this study are calcium carbonate, barium sulphate, ultramarine and cellulose from pure compounds recorded on my instrument. FTIR gives the most convincing proof for Prussian Blue and these other compounds.

Reflectance spectroscopy records the light reflected from the surface of stamp when white light impinges on the surface. The pigments in the ink will absorb (remove) specific bands of colour from the white light. Thus a blue coloured stamp will have pigments that remove the greens and reds from the white light and will show a peak reflectance in the blue end of the reflectance spectrum (400-475) nm. This is the case for the blue stamps studied here. Reflectance spectroscopy is not an excellent diagnostic technique for segregation of shades in stamps. Small variations in ink density, stamp paper whiteness, paper and pigment aging along with environmental factors will alter the reflectance profile and give the impression of shade differences. However, significant peak shifts and profile differences do signal a shade change.

Some specific comments on the analysis of each issue:

Columbian Issue: All three spectroscopies confirm that the 4¢ error has the same chemistry/spectra as the 1¢. The FTIR of the error shows the diagnostic peat at ~2100 cm^{-1}. The FTIR shows high iron and the reflectance curves of the 1 4¢ and the 4 4¢ error are very similar and different from the 4¢ normal. The Columbian error is an excellent choice to show not only that an error exists but why it occurred.

NFLD Issue: I was approached by John Walsh to look at the Prussian Blue error for this stamp. He felt though his study of the production and history of this issue the error did not exist. He was able to borrow an APS certified copy along with about 10 other borrowed copies. Garfield Portch of the VG Greene Research Foundation was looking into quantifying their Prussian Blue reference copy with reflectance spectroscopy. He kindly supplied their reference copy along with three normal copies. I performed the FTIR, XRF and Reflectance study that is detailed in the paper by the three of us and in the paper by John Walsh (see reference section). The conclusion reached is the same as presented in this exhibit: shade variations do occur due to ink density and more importantly, to the particle size of the Prussian Blue pigment. As detailed in the paper by Semain (see reference section) Prussian Blue pigment can be prepared by multiple processes that give different particles sizes that in turn give subtle tinting to the basic blue shade. The Greene Foundation continues to certify a reflectance spectrum match to their reference copy as a Prussian Blue variety. I have NOT included the samples from John Walsh or Garfield Portch as I returned them to their owners. Furthermore, I did not include their spectra in the analysis of my copies as the XRF and reflectance spectra were recorded under different experimental conditions. Instead, I purchased a RPSL certified copy and compared it to 22 'off the shelf' copies and came to the same conclusion as before. It is up to the philatelist to decide if a visual and or reflectance difference constitutes a bone fide Prussian Blue shade but from a purely analytical approach, the exhibit shows no substantial difference between the certified copy and the others.

United Nations Issue: The monograph by Kvarnes (see reference section) is definitive in stating that the "*the First Issue has one true color error - the Prussian Blue 15 airmail. During the initial color check of the printing run of the 5th printing, the ink was found to be far different from the intended color and this was corrected. About 100 sheets (5000 stamps) by mistake got included in the shipment and were placed on sale without notice by the UNPA. The color is quite distinctive, since the vermilion is missing. This color error is of sufficient degree to merit a separate space in addition to the one for the ordinary 15~ airmail stamp in some German albums*." The cause of the colour error described above may or may not be true. However, the exhibit shows unequivocally two distinct ink chemistries were in use during the 11 year production period. The error described above occurred when Prussian Blue was left out of the formulation. Not mentioned in this exhibit is the hypothesized addition of lead chromate to the error ink formulation to match the previous shades. Both lead and chromium are seen by XRF in the error ink and not in either of the other two inks. As of the writing, I have not been able to confirm the presence of the compound lead chromate in the FTIR spectrum. Computer simulations show that the shade of the error can be approximated with addition of chrome yellow (lead chromate) to ultramarine along with some carbon black. The addition of vermillion (mercury sulphide) is not supported by this research as mercury is not seen in the XRF spectrum. The monograph by Kvarnes makes extensive use of the eye-observed fluorescence of the paper to date the issues. He claims six distinct fluorescent intensities and glow. However I have been able to partition the fluorescence by wavelength into two or at best three types. The exhibit used only two partitioning and has used dated covers. I feel that this is the preferred method.