The Chemistry of the War Time Admiral

A spectroscopic study of the red 2¢ Admiral Issue of Canada
and
The identification of a WW I shade solely defined by its spectroscopy

This paste-up coil was produced around May 11, 1915 during the First World War. Most viewers of this stamp will see two distinct shades. But getting philatelists to agree on the names of these two shades has always been a problem. Even with color guides, most collectors would have trouble matching shades to names. This study will address this problem by using three spectroscopic techniques to show that these changes in shade have occurred due to changes in ink chemistry. Furthermore, it will show that a broad grouping of shades can be done from its spectroscopy alone. An aniline pink shade will be shown to have a unique spectroscopic signature.

Image of the Gum Side of the Past-Up Coil (x 1.25)

Organization and Objectives

Section 1: Pages 2-4. Reflectance Spectroscopy: Examples from the entire Admiral series are used to illustrate this type of spectroscopy. Next, the continuum of shades of the 2¢ red carmine are shown to be partitioned into two major groupings based on spectra. Finally, through plate blocks, the dating of the shade transitions is shown.

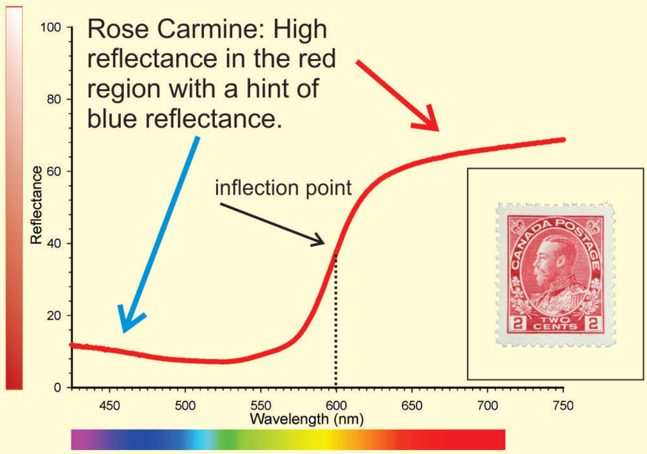
Section 2: Pages 5-8. X-Ray Fluorescence (XRF) and Fourier Transform Infra Red spectroscopy (FTIR): These are used to show the changes in the ink chemistry that caused the changes in shade. Elements present in the ink are identified by XRF while chemical compounds in the paper and ink are found using FTIR. The major changes in ink chemistry occurred during WW I.

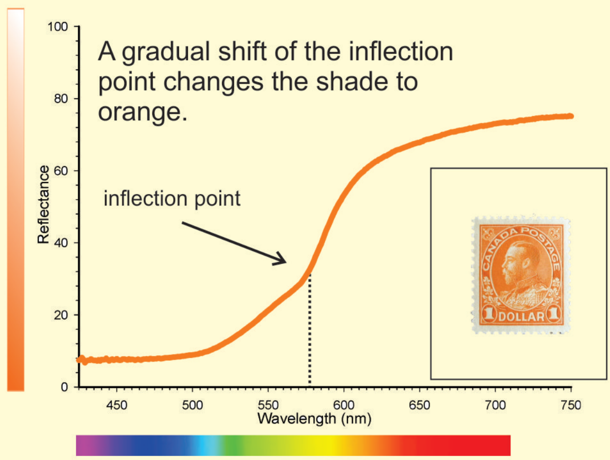
Section 3: Pages 9-10. A Flow Diagram and the 'Aniline Ink' Variety: The section details the steps in the production of a quality printing ink at the turn of the 20th century. It identifies the location at which the various compounds enter into the ink making process. It pinpoints the likely reason for a production flaw that causes a serious bleed through of the ink to the gum side ('aniline ink').

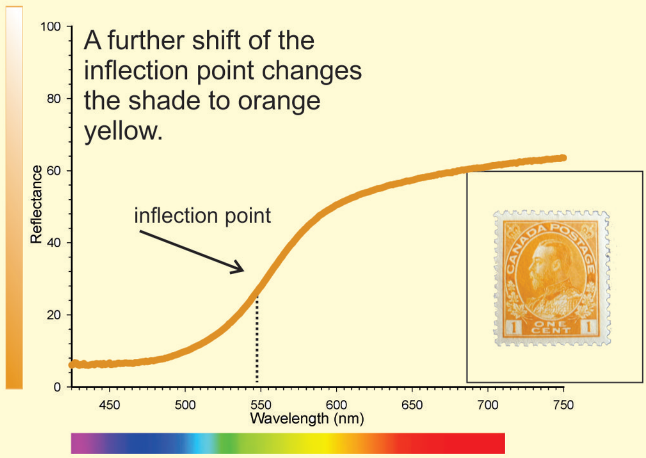
Section 4: Pages 11-13. The 'Aniline Ink Pink' Shade: Five expertized stamps certified as pink have a chemistry that is pre WWI and very similar to certified rose carmine stamps. Two other certified pink stamps are part of a group of only 2.3% of the 468 in this study. This group has unique features in both their reflectance spectra and chemistry. This group is called the 'aniline pink' shade as detailed in this section.

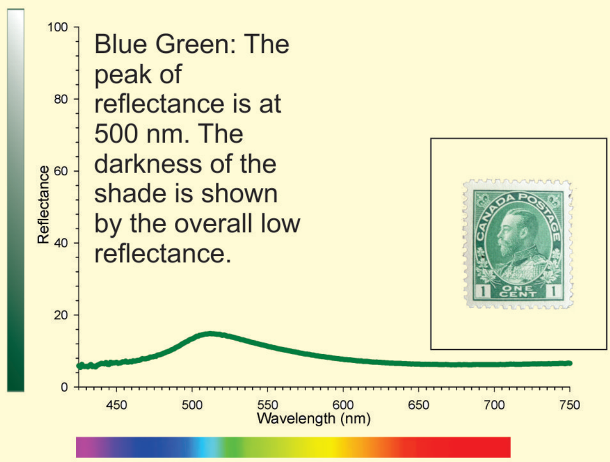
Philatelic Interpretation of Reflectance Spectra

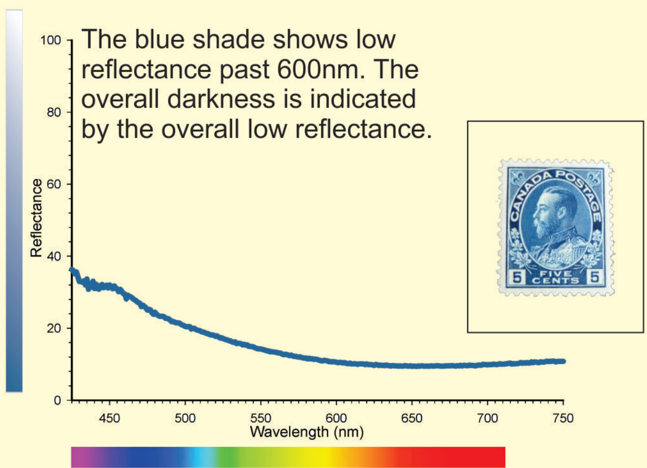
A reflectance spectrum is a graphical representation of what your eye perceives as the color of a stamp. Each person looking at the same stamp will have their own interpretation of the shade. Frequently, no two individuals will agree on the name of the shade even if a color guide exists. Not so of an reflectance spectrum since a properly calibrated spectrometer in any lab will produce the same spectrum. Below, one can follow the major changes that occur in the spectrum for six Admiral stamps of widely different colors. At the bottom of each graph is the color associated with each position on the wavelength axis. The reflectance spectrum is very sensitive to small changes in shade. Thus, it is difficult to use reflectance spectroscopy alone to match stamps that the eye preserves as identical shades since the spectra may have distinct differences.

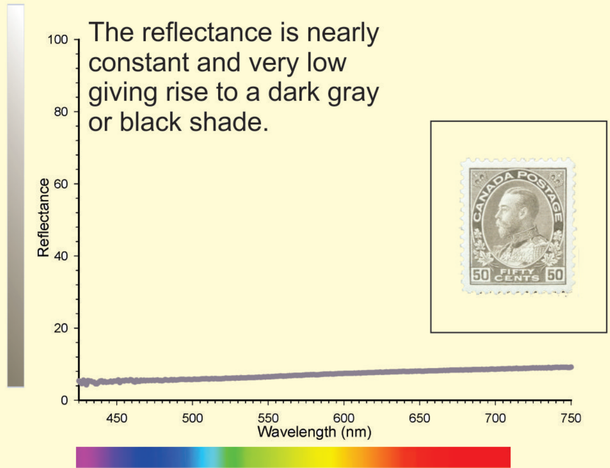






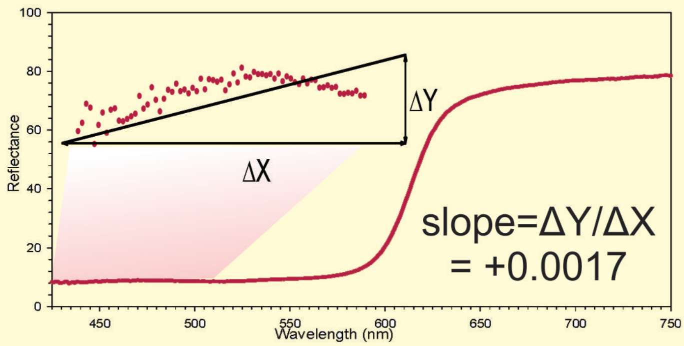




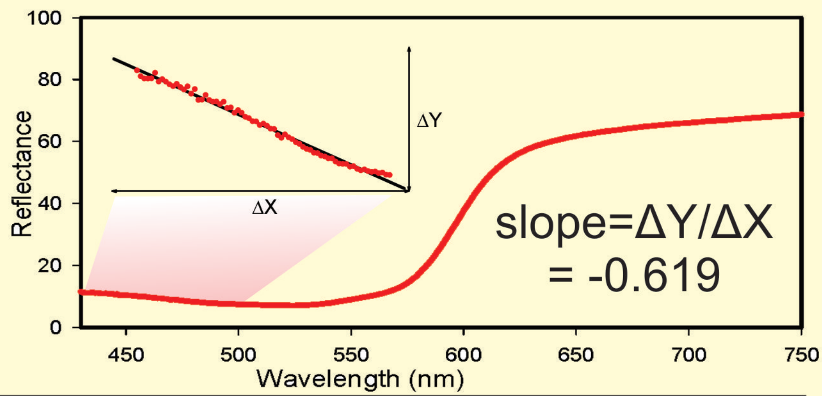


Reflectance Spectra of the Two Major Shades of the 2¢ Carmine Admirals

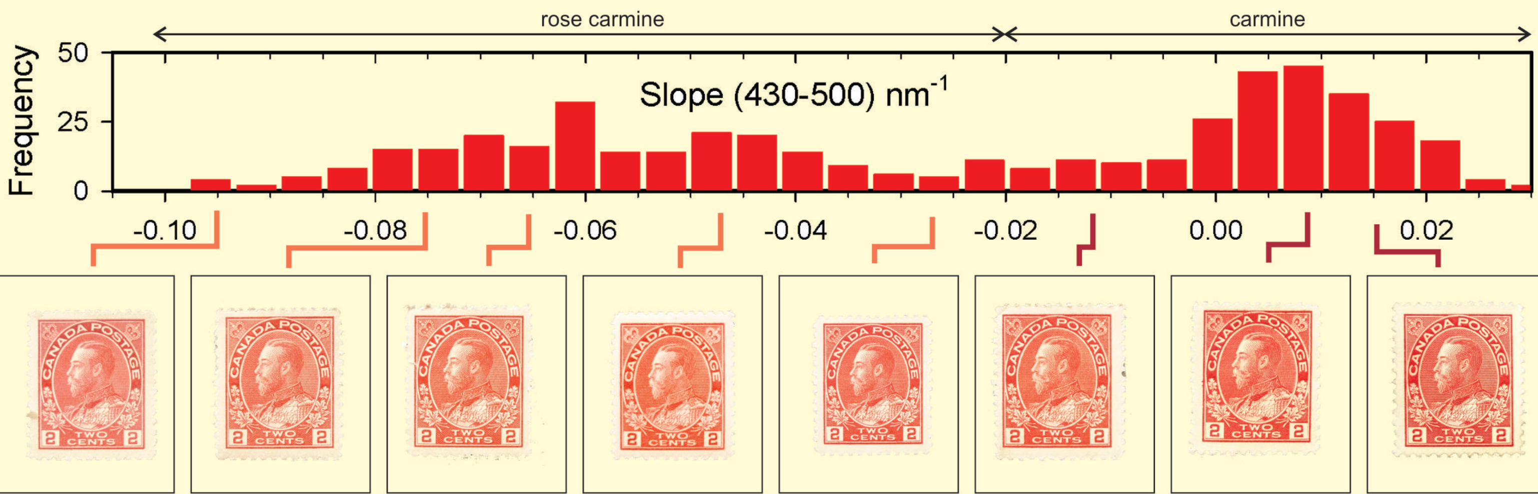
A feature that is correlated with the differences between the two major shades is the tilt or slope of the reflectance spectrum from 430 nm to 500 nm as show in the inset. For the ***carmine*** plate block (Plate 160) below, the line tilts very slightly upward (the slope is positive and small). **Plate 160 was the last of the 2¢ carmine plates produced**.



The tilt of the line in the region between 430 nm and 500 nm for ***rose carmine*** is tilted downward (the slope is larger and negative). **Plate 4 is the well known 'hairline' variety that shows well defined horizontal thin lines of ink that span the entire plate.** It is part of the very early printing of this issue.

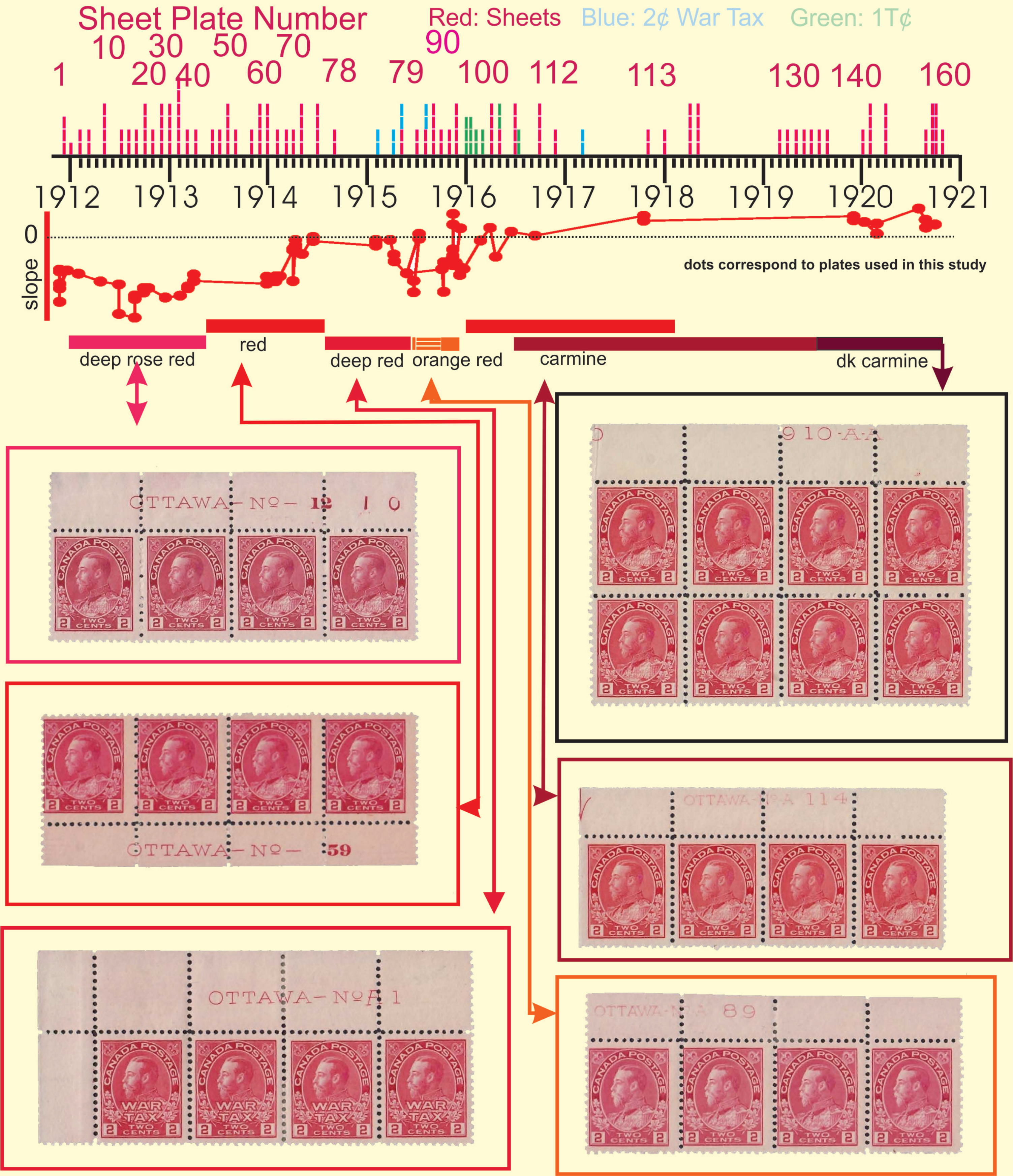


For this study, the slopes of approximately 460 mint stamps and plate blocks were measured. The contribution to the population by blocks of stamps was counted as a single stamp for each block. The histogram below shows the number of stamps that fall into each of 30 ranges or buckets that span the slope range. The histogram shows that a continuum of shades is present but does show a weak bimodal distribution into the rose carmine and carmine shades of the Scott catalogue.



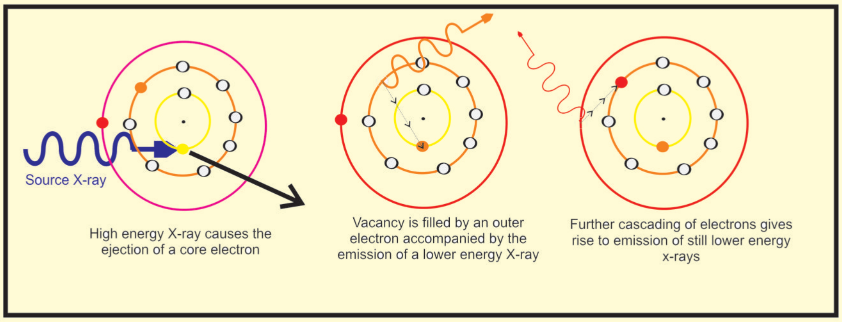
Dating the Changes in Slope From Plate Numbers

Around plate 69 (May of 1914) the slope of the reflectance spectrum started its migration to positive values with the period up to plate 99 (Mar, 1916) showing wide swings. Leopold Beaudet has kindly supplied the colour designations shown below matching plate number with the Unitrade catalogue shade designations. Note the intermediate shades of deep red, orange red and red are in the this transition period.

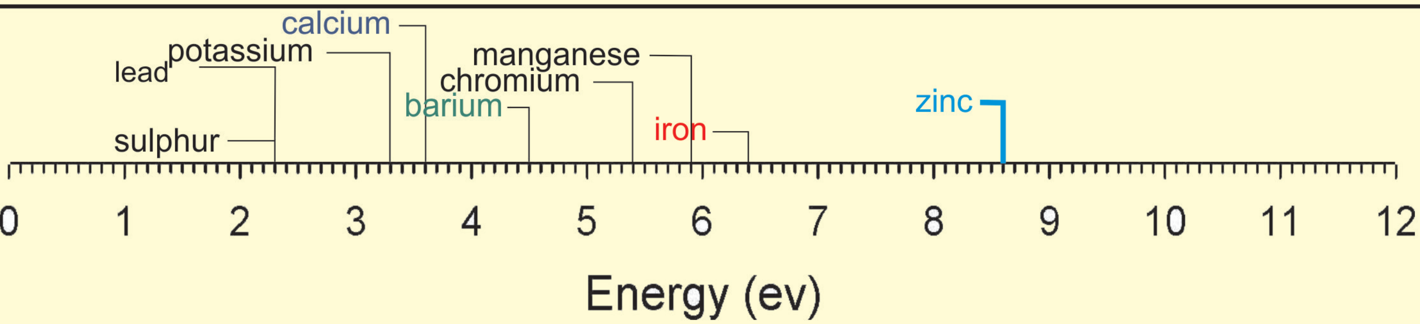


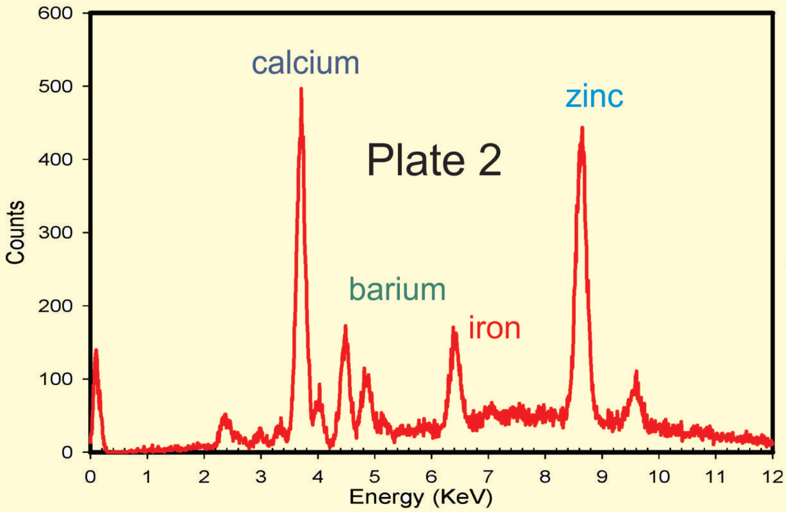
Philatelic Application of X-ray Fluorescence (XRF)

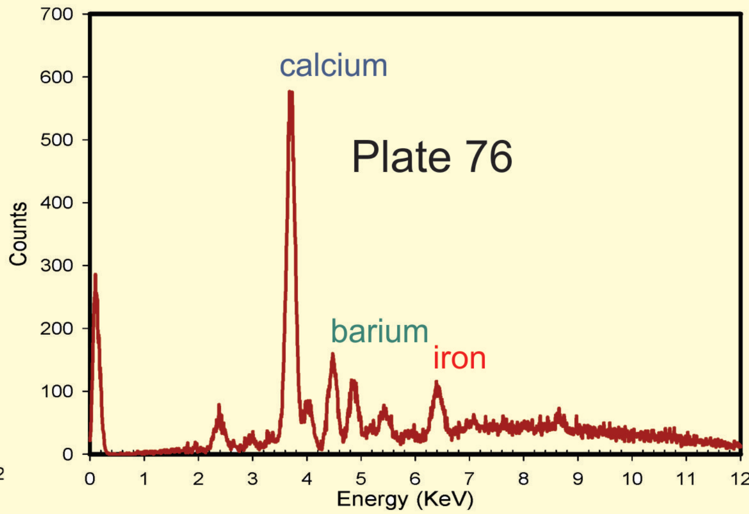
The changes in the shades of the 2¢ Admiral is a consequence of the changes in the composition of the ink. An X-ray Fluorescence spectrum is a powerful tool that can be used to monitor the chemical change without damaging the stamp.



When excited by X-rays, the various elements in the chemical compounds in the ink will interact with the in-coming X-rays. Each element present in the ink will eventually emit light of an energy that is characteristic of that element. Only those elements indicated below have been found in the stamps in this study although not all stamps have all elements as seen in plates 2 and 76 where Zn has disappeared.

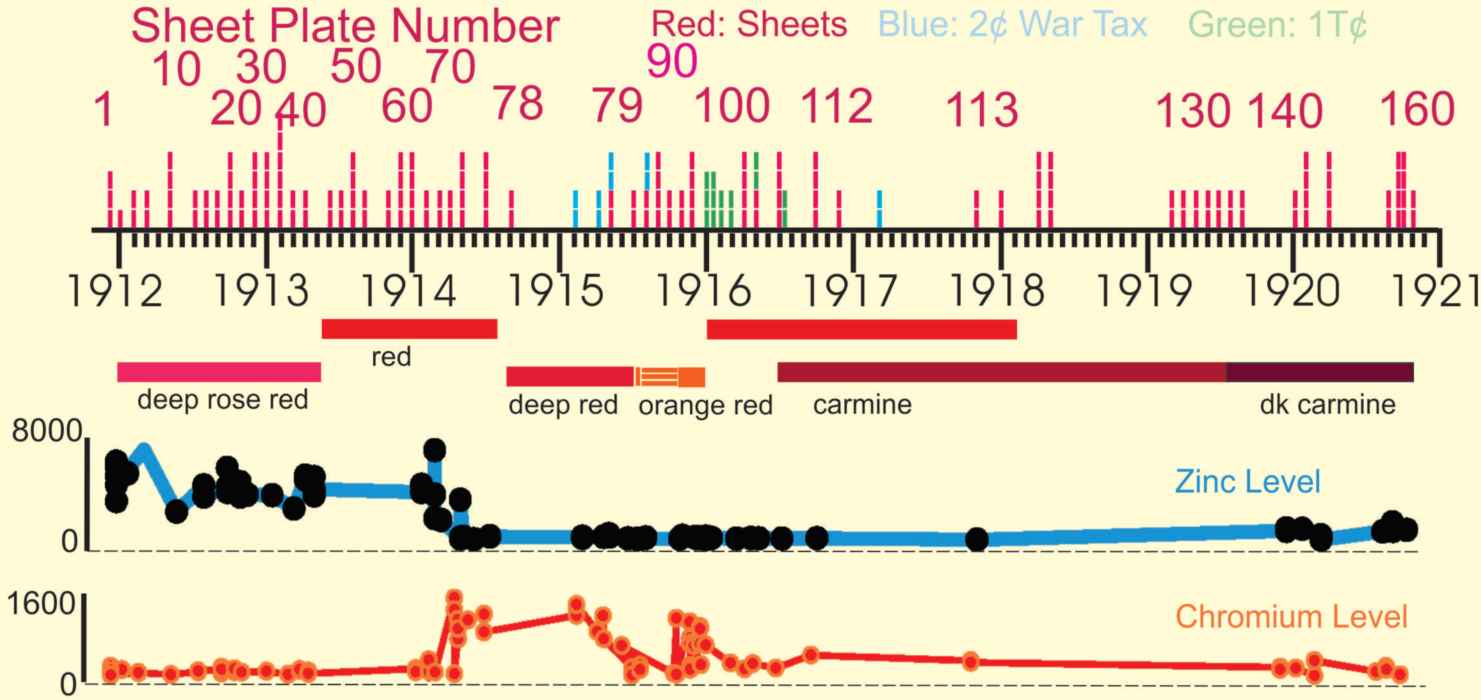






Dramatic Changes in Ink Chemistry at the Start of World War I

From the plate numbers on 81 plates measured in this study, the changes with time in the ink levels of the elements zinc and chromium can be followed. The pre-war high levels of zinc disappear while chromium levels make an erratic appearance around March of 1914.



Plates 66 and 67 are separated by only 50 days yet the levels of chromium and zinc are very different. Plate 66 has typical zinc and chromium levels seen in stamps produced pre-war. Plate 67 has no zinc and high chromium levels. Zinc is absent from early 1914 until the end of the war and very low or absent onward. Chromium levels were highly erratic from the start of WW I to around 1916. Plate 67 has an exceptional high chromium level. Nonetheless, the shades are similar to the eye.

Zn:1759 , Cr:121

Zn:104 , Cr:1599

Plate 68 was approved for use on April 22, 1914. The actual date of use would be somewhat after that date. Marler reports the earliest known cancellation for plates 65-68 is August 21, 1914. Zinc compounds were available during a part of plate 68's production period. The shades are very different. Is this due to changing levels of zinc and chromium or are shade changes due to a third factor that cannot be seen by XRF? ***Additional and critical information is provided by Fourier Transform Infrared spectroscopy***.

Zinc was a strategic material during WW I which accounts for its disappearance.

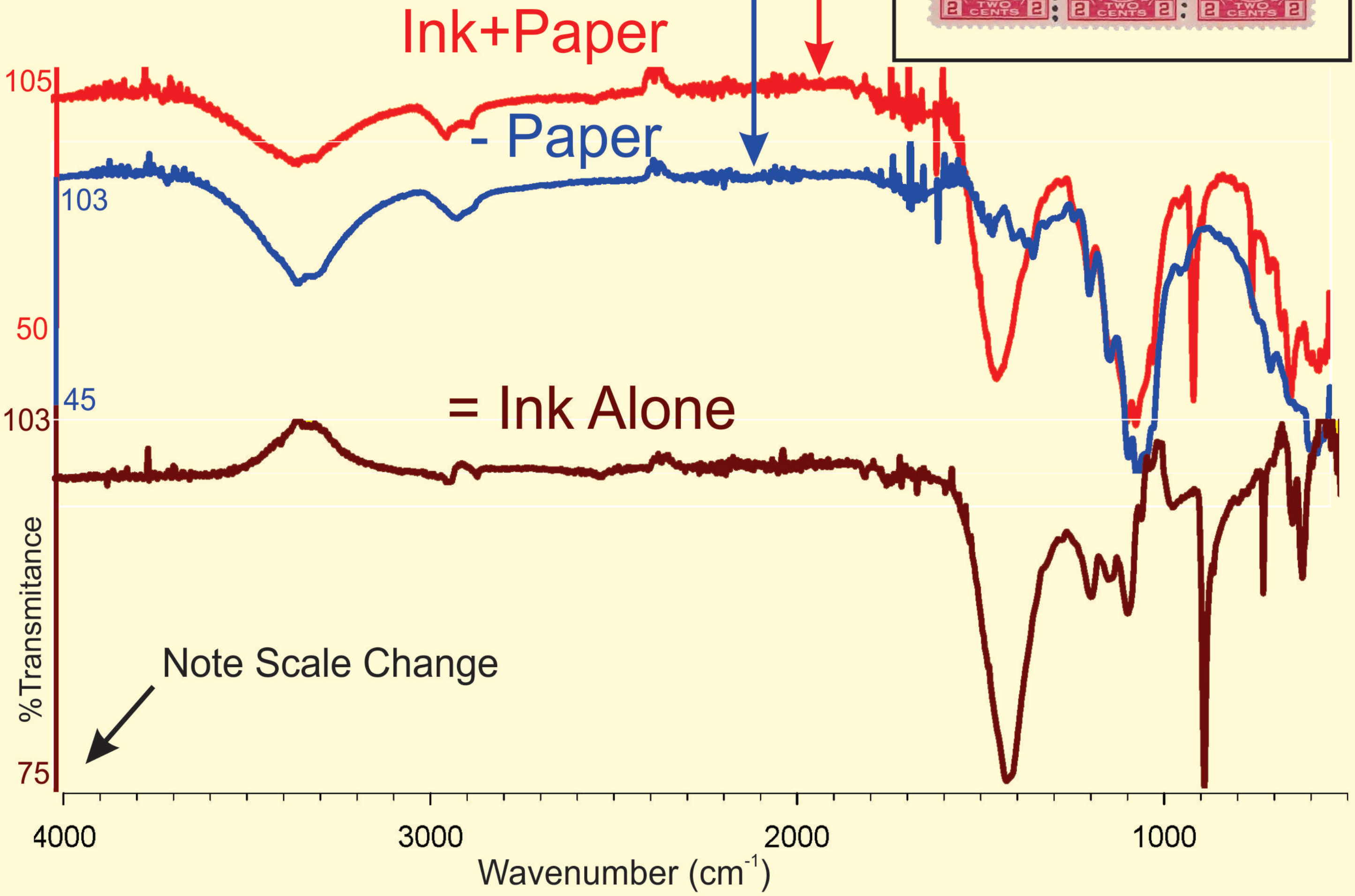
Zn:3549 , Cr:91

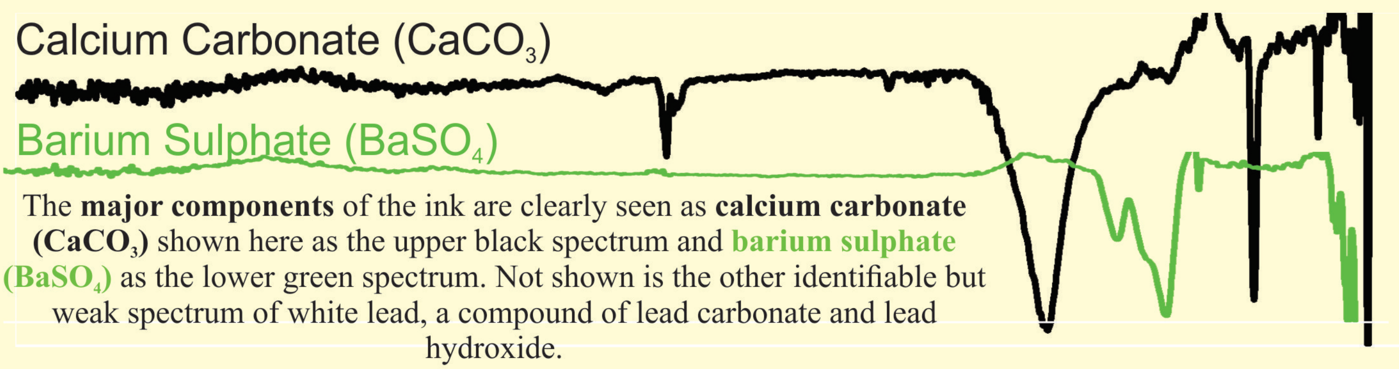
Zn:145 , Cr:1361

Infrared Spectroscopy of a War Tax Admiral

The X-ray spectra of the Admirals will only give information about the elements present in the ink, not on how the elements are bonded to form compounds. Infrared spectroscopy will allow the identification of the molecular or ionic compounds present. In the case of complex mixtures such as printing inks, the classes of compounds present rather than the actual compounds are more likely to be identified.

The IR spectrum of the selvage area will give information about the paper alone. The spectrum of the portrait and border portion of the stamp has contributions from both the ink and the paper. The paper can be easily subtracted out digitally to give only the contribution due to the ink alone.

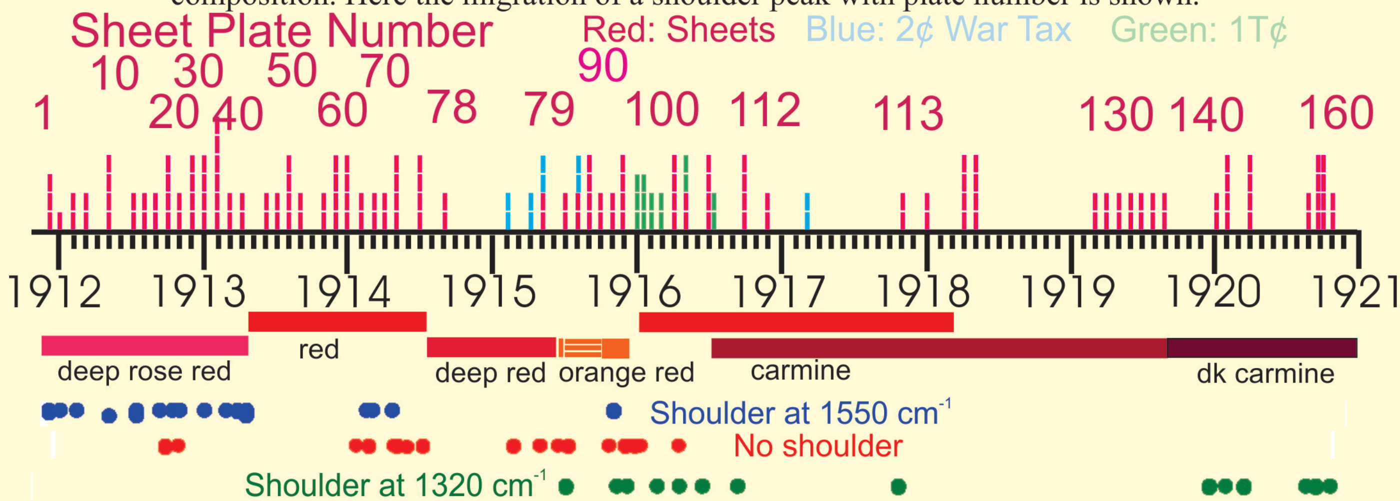




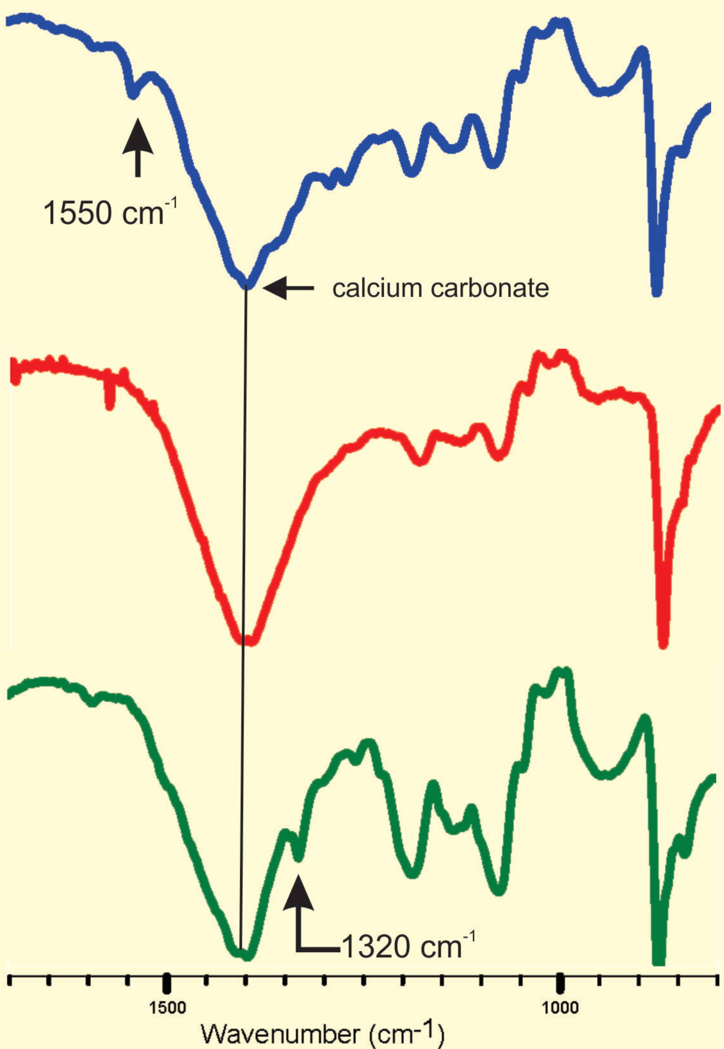
The **major components** of the ink are clearly seen as **calcium carbonate ($CaCO_3$)** shown here as the upper black spectrum and **barium sulphate ($BaSO_4$)** as the lower green spectrum. Not shown is the other identifiable but weak spectrum of white lead, a compound of lead carbonate and lead hydroxide.

The Changing IR Spectrum

Although only a few major chemical compounds are found in the ink of the red Admiral stamps, the subtle changes in the IR spectrum with time can be useful in correlating shade changes with changes in ink composition. Here the migration of a shoulder peak with plate number is shown.



A peak distortion is seen when weaker absorption by a second compound underlies the absorption profile from a major chemical component, in this case calcium carbonate. A shoulder appears at 1550 cm^{-1} for the majority of pre-WW I plates (deep rose red, indicated in blue, above). The shoulder at 1320 cm^{-1} is found for both WW I and post-WW I plates (carmine shades, indicated in green above). A broadening of the major peak is seen primarily for the WW I shades (indicated in red above). This migrating shoulder is likely due to the use of three different red dyes in the manufacture of the ink. The change in dyes was necessitated by the unavailably of the high quality German manufactured dyes during the war and post war periods.



Ink Production

The Role of Dyes

The color of a stamp is determined mostly by the choice of dye. For this issue, there appears to be three major dyes in use.

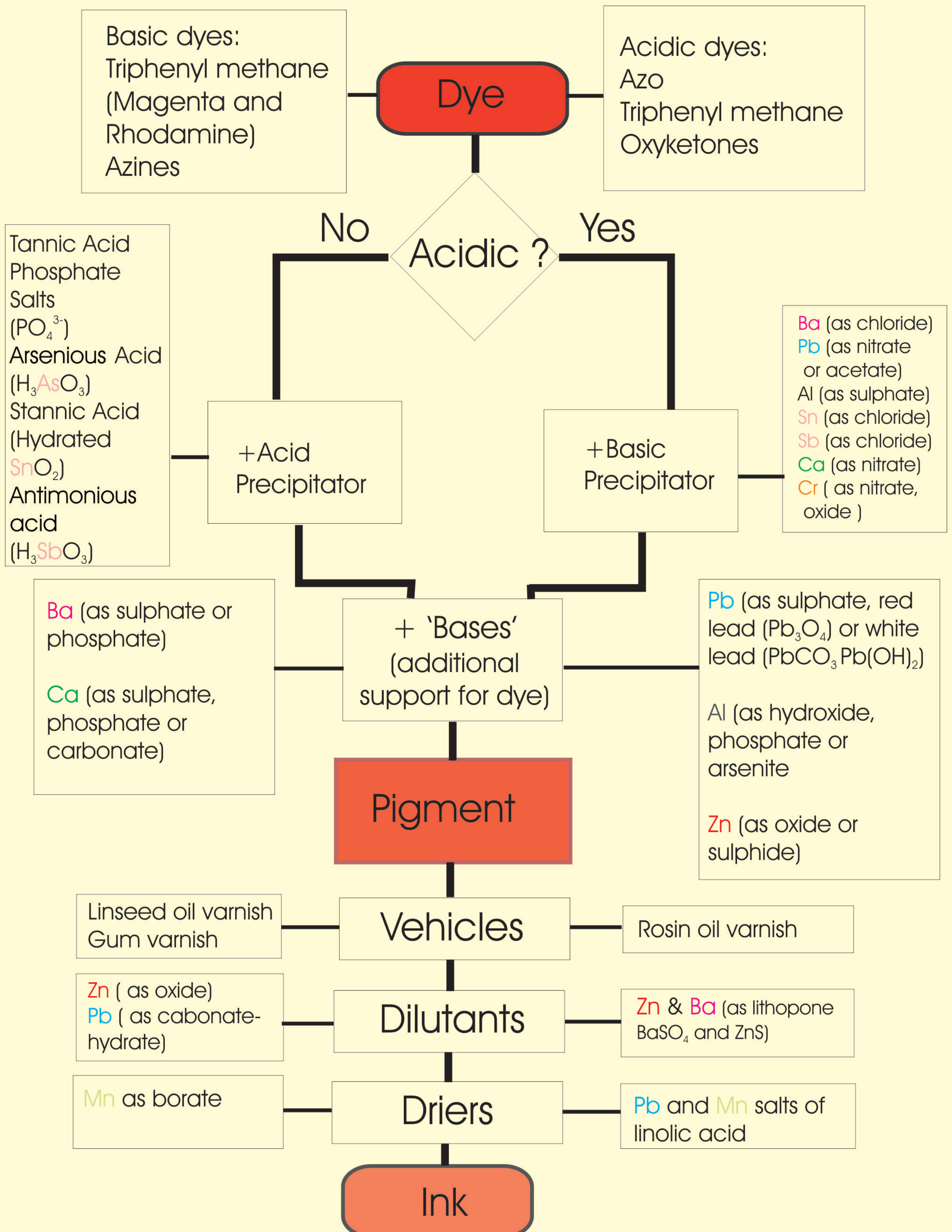
no shoulder

shoulder at 1550 cm^{-1}

shoulder at 1320 cm^{-1}

The Role of Dilutant Chemicals

Many factors contribute to the perceived shade of a stamp: (a) The whiteness of the paper (b) whether the plate has been over or under inked (c) changes to the depth of the engraved lines due to wear (ink density) (d) changes in the color strength of the base pigment. The base pigment is strongly absorbing and deeply coloured. To arrive at a consistent shade and to compensate for effect (d), printers add white pigments to dilute the intensity. The stamps from Plate 4 offer an opportunity to look at the effect of the dilutants. Plate 4 is easily identified by the numerous hairlines throughout the stamp. If it is assumed that the same chemical compounds were used to make the red pigment over the plate's use then we can assess the success of the printers in maintaining a constant shade. Below are eight stamps with widely different ratio's of calcium : barium : zinc : lead (four elements whose chemical compounds are white).

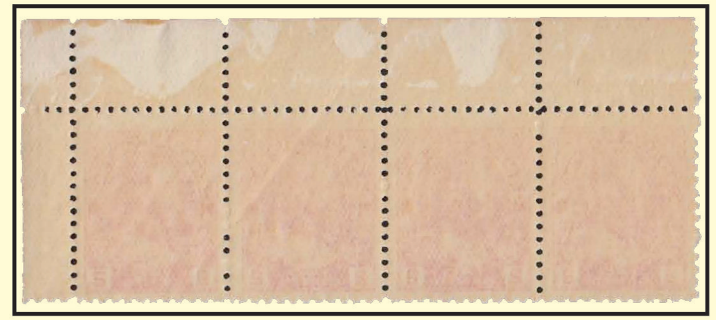


When Things Go Wrong

The dye is soluble in water. To form a solid, insoluble pigment, the dye is precipitated with various agents. If not done properly, the pigment becomes partially soluble. Since the 2¢ Admiral was printed on damp paper, this defect shows up as a bleed through of the pigment to the gum side of the stamp.

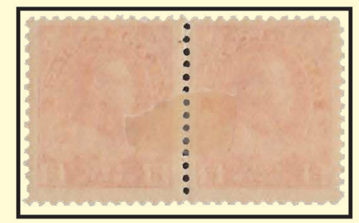
Pre-war stamps were generally free of this defect although some slight bleed through occurred around plates 17 and 20 as shown here.

x0.75



More frequent and more severe bleed through occurred at the start of the war and continued for about a year. At which point, a more stable pigment became available. Below, is an example of a WW I era pair.

x0.75



The Role of Dryers

Manganese compounds enter as agents to hasten the drying of the ink on paper. The levels are variable and appear throughout the production period.

Mn 1610
Pre War

Mn 983
War

Mn 477
Pre War

IR and XRF Analysis of the Aniline Ink Variety

Show a likely change in dyes and a link to chromium levels

The earliest Pre World War I printings that showed substantial bleed through occurred in plate 17. Shown below are a bleed through and normal variety. The chemical element composition is virtually identical in both printings. The FTIR spectrum however shows the disappearance of the shoulder at 1550 cm-1 in the aniline ink variety suggesting a change to an inferior dye used for a short period. The element chromium is not present in stamps produced up to the start of WW I. The other reported pre WW I aniline ink variety is for plate 37.

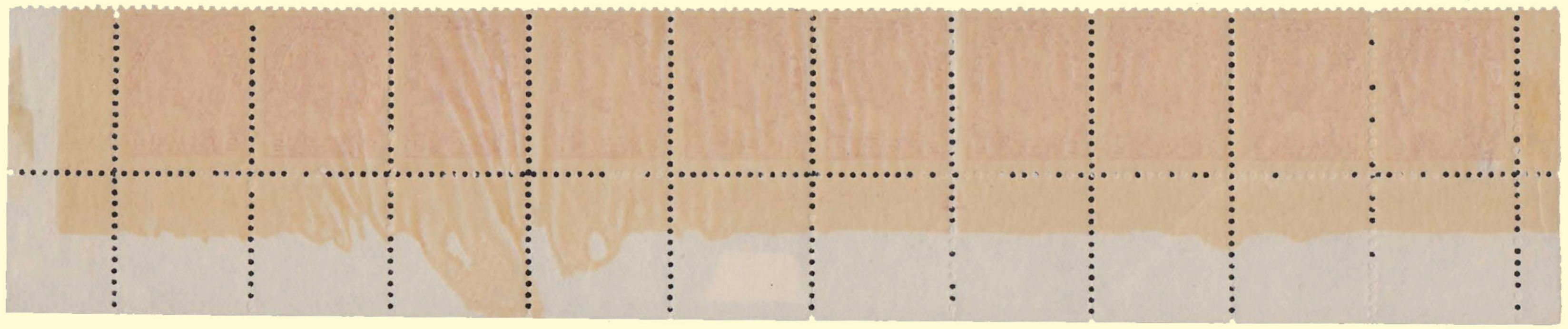


Plate 17 Aniline Ink

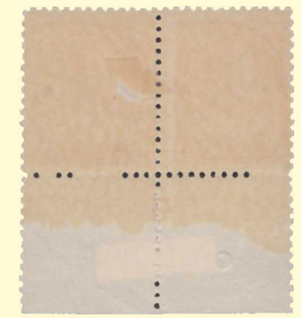
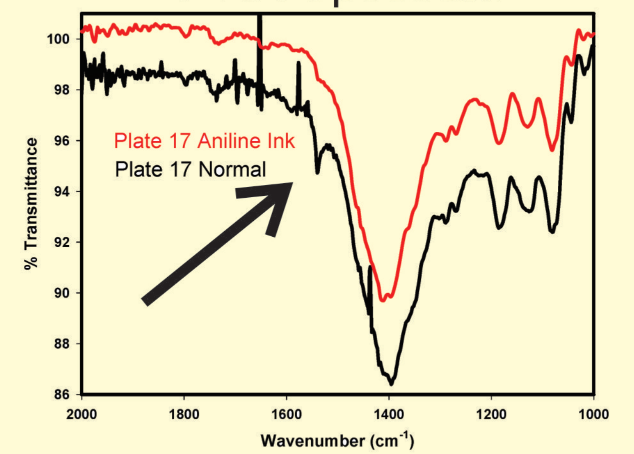


Plate 17 Normal

Elemental distribution in the aniline ink(red) and normal (blue) plate 17

zinc	4700	4700
calcium	6050	6311
barium	2431	2769
iron	1061	1504

FTIR Spectrum

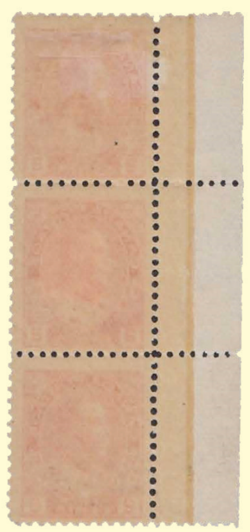


Scan of the portrait side reduced to 75%

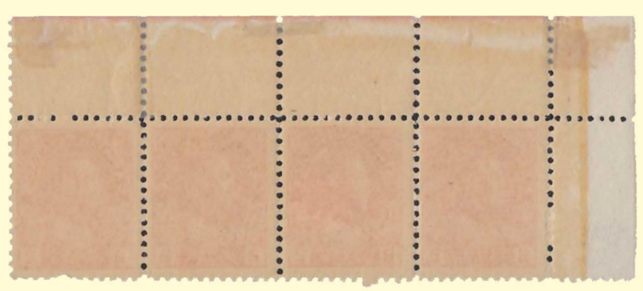
Scan of the portrait side reduced to 75%

- Quality German pigments became unavailable at the start of WW I. The substituted dyes and pigments were of inferior quality and bleed through of the ink to the gum side became a problem. There is a correlation between the chromium (Cr) levels (reported as counts per second) and the degree of bleed through. Stamps of very low Cr levels show the most bleed through.

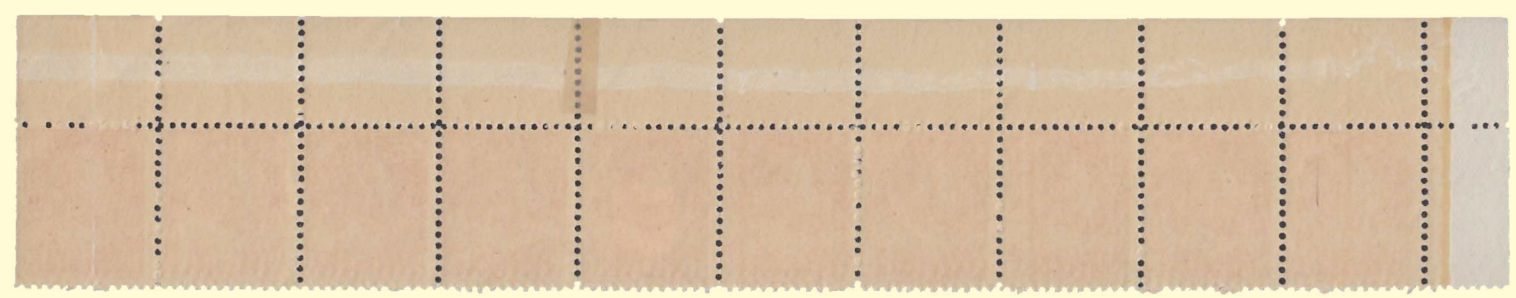
All scans of the portrait side reduced to 75%



Cr: 151



Cr: 207



Cr: 647

Conclusions Based on Spectrosopy

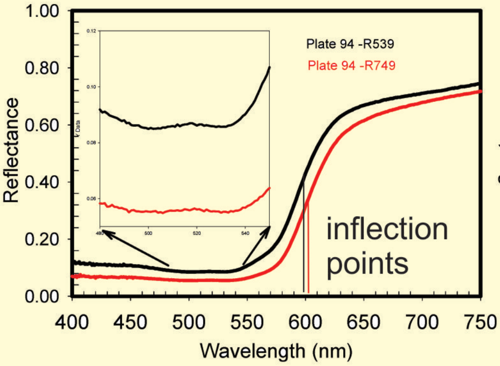
- The reflectance spectra show that a continuum of shades exists. The histogram on page 3 of the exhibit indicates that two major shades make up the bulk of the population.
- X-Ray spectra show that a compound containing zinc disappears at the start of World War I. The element chromium makes an appearance at this time but the levels are erratic. There is no apparent connection between chromium levels and shades as shown on page 6.
- The Infrared spectra show that the compounds barium sulphate, calcium carbonate and white lead are present in all stamps. These compounds cannot account for shade variations as they are all pure white. The contribution by zinc is either from zinc sulphide or zinc oxide but overlap by the other compounds prevents positive identification. There is a migration of a shoulder peak that does parallel the transition of shade from pre and post WW I shades. A possible assignment of these shoulder peaks is to a change in dyes used during this period.

The Case of Plate 94

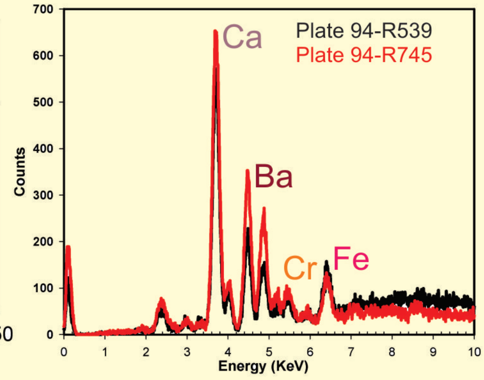
This study has not produced a ‘smoking gun’ that can identify a shade with a particular feature in *all three types* of instruments used here. For example, plates 94-R539 and 94-R745 have nearly identical XRF spectra as seen in the middle plot. The IR spectra are remarkably similar (plot, far right). The major difference is only in the reflectance spectra which does parallel the perceived shade difference. Part is due to the shift of the inflection point to the right of the plot, the other is the slight curvature of the black plot near 520 nm shown in the inset. What is not known is the cause of the shift and the small bump. It is likely due to differences in the red pigments whose absorption profile is hidden under the strong calcium carbonate peak at 1400 cm^{-1} in the FTIR spectrum (far right). This small bump however is a starting point for the identification of a shade that is difficult to identify, the pink shade.

R539

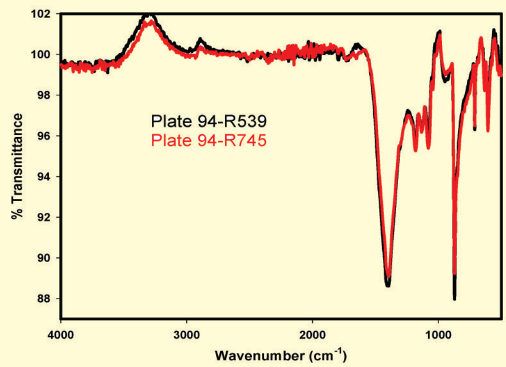
R745



Reflectance Spectrum



X-Ray Spectrum



Infrared Spectrum

Grouping of Certified Stamps by Spectroscopic Properties

The slope of the spectrum from 430 to 500 nm is calculated from a fit to a linear equation of the form

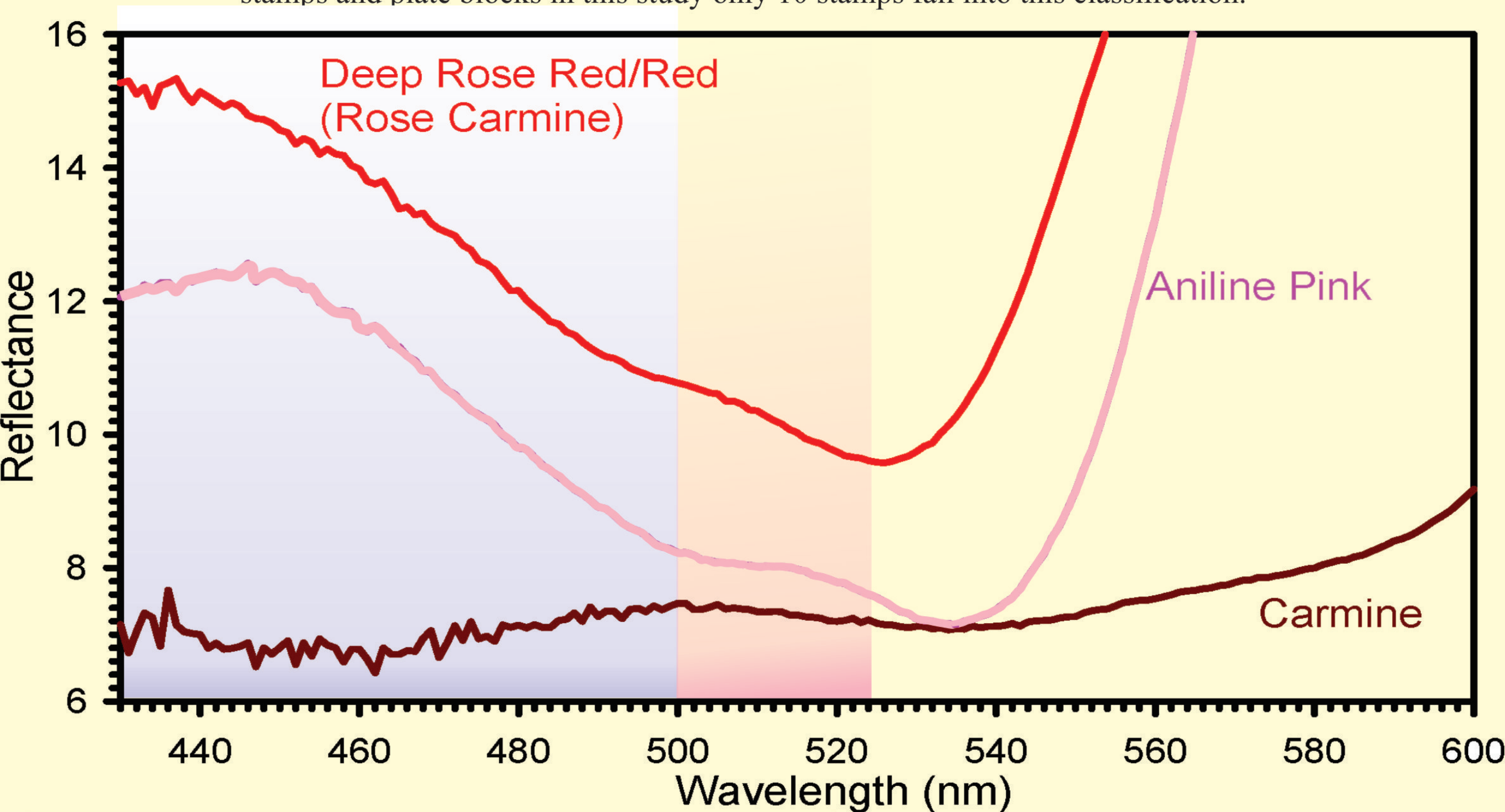
$$\text{Reflectance} = a_0 + a_1 \bullet \text{wavelength}$$

Large negative values of a_1 visually correlated with the deep rose red shade while near zero or positive values are seen for the carmine shade.

The middle reflectance spectrum shown below had a noticeable 'bump' near 512 nm. This deviation from linearity can be measured by fitting the region from 505 to 525 nm to a quadratic equation

$$\text{Reflectance} = b_0 + b_1 \bullet \text{wavelength} + b_2 \bullet \text{wavelength}^2$$

The more negative the b_2(quadratic) term, the more noticeable is the bump. Stamps with a linear term, $a_1 \leq -0.040\ nm^{-1}$ and a quadratic term, $b_2 \leq -0.0019\ nm^{-2}$ select out a very small subset of the deep rose red stamps that have a distinctively unique shade that here is called aniline pink. Of the 469 single stamps and plate blocks in this study only 10 stamps fall into this classification.

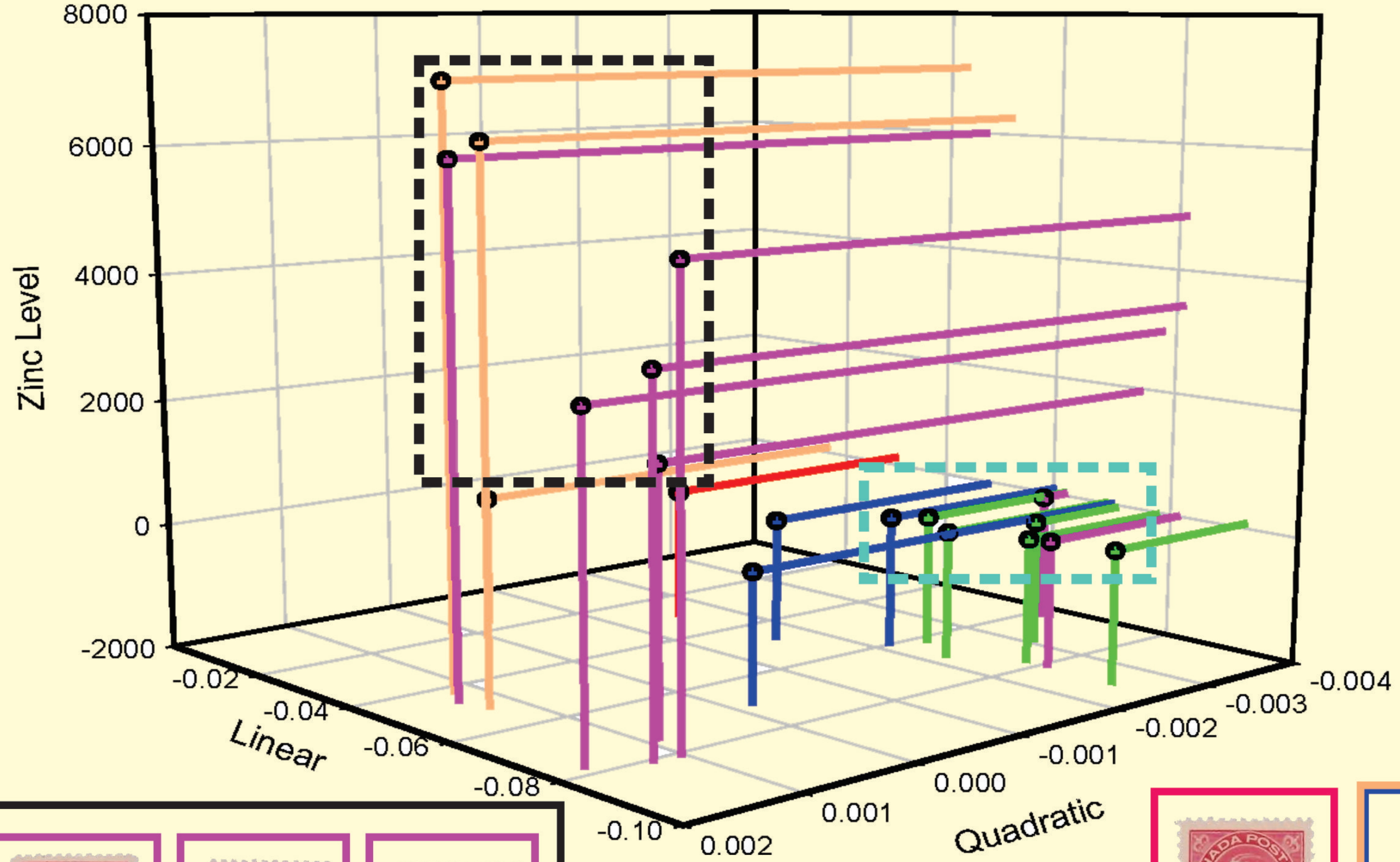


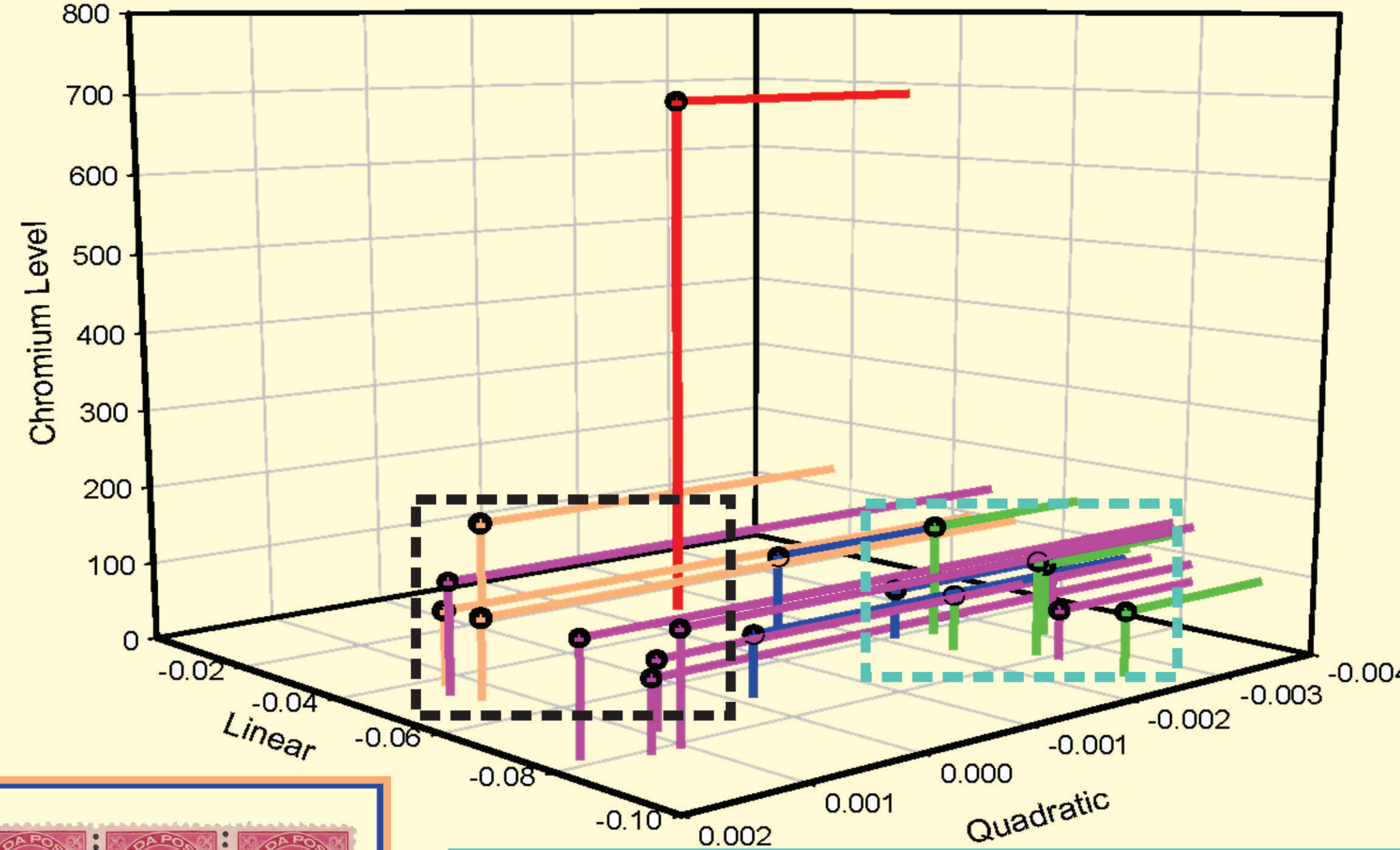
Deep Rose Red

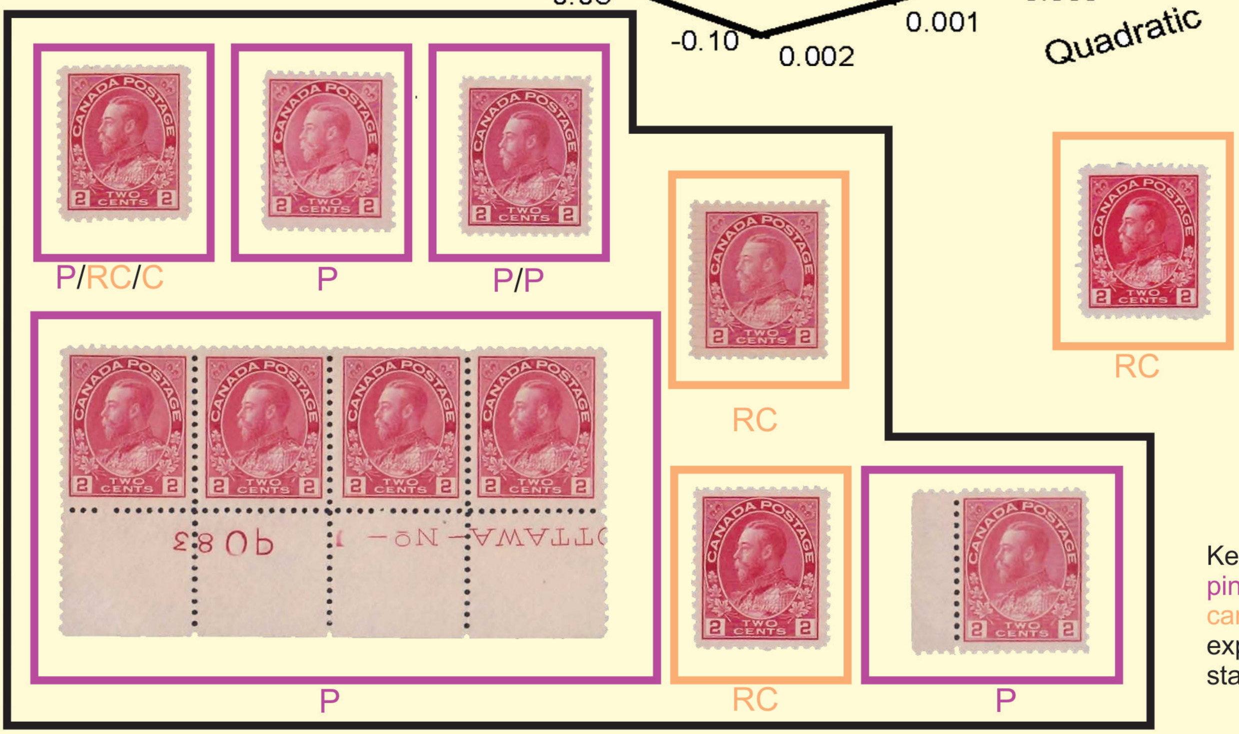
Aniline

Carmine

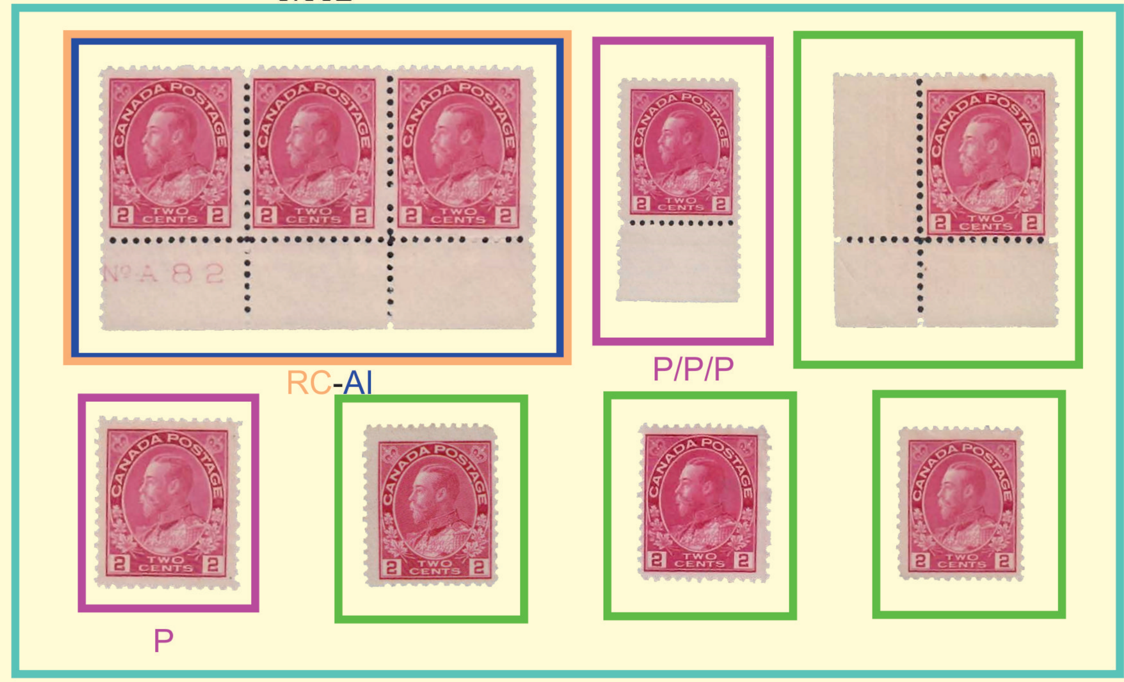
Shade Grouping by Reflectance Spectroscopy and XRF Spectroscopy







Key: Stamps outlined in: Pink are for expert certified stamps as pink shade, Orange are for expert certified stamps as rose carmine, Blue for expert certified as aniline ink, Orange-Red for expert certified stamps as orange red and Green for uncertified stamps. Some stamps have multiple certificates as indicated by /.



The large enclosing dotted rectangles in both graphs (top row) have grouped stamps by like spectroscopic properties. The stamps in the black dotted rectangle have pre-WWI levels of zinc and chromium, ***positive* quadratic coefficients** and large negative linear coefficients. Contrast that with the seven stamps shown in the enclosing turquoise rectangle All have **large *negative* quadratic coefficients**, large negative linear terms and WW1 type Cr and Zn chemistry. The stamps certified as pink in the black rectangles do not have a different chemical makeup of the large number of pre WWI stamps analyzed in this study. The two certified pink stamps in the turquoise rectangle, the four uncertified stamps along with the aniline ink plate block form a very small subset of the stamps in this study, all with a quadratic coefficient smaller than -0.0019. **This study has found that stamps that fall into the later classification for a unique shade for this issue. The term aniline pink is suggested for this grouping as most stamps show significant bleed through.**