Chemistry of Aniline inks, 2-cent Admiral Issues of Canada

Richard Judge
London, UK
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Canadian Admirals (Summary)

- The regular issue of the Canadian Admiral series sheet stamps were produced from the late 1911 to late 1927.
- Shades range from as many as 8 for the 2₵ carmine to as few as 2 for 5 different denominations. (Unitrade Catalogue).
- Early printings was on wet paper but starting on Dec of 1922, printing was on dry paper.

Admiral Shades

dark green
blue green
yellow green
dark yellow green
(4)

orange yellow
lemon yellow
yellow
pale yellow
(4)

yellow green
green
deep green
(3)

carmine
rose carmine
pink
deep rose red
dark carmine
rose red
deep red
red
(8)

brown
yellow brown
dark brown
(3)

carmine
rose carmine
(2)

olive bistre
olive yellow
golden yellow
yellow ochre
(4)

dark blue
indigo
gray blue
(3)

violet
gray violet
rose violet
(3)

yellow ochre
olive bistre
straw
sage green
greenish yellow
(5)

red brown
pale red
brown
(2)

blue
light blue
(2)

plum
reddish purple
(2)

blue
light blue
(2)

bistre brown
yellow brown
(2)

olive green
sage green
dark olive green
gray green
(4)

black brown
black
silver black
brown black
(4)

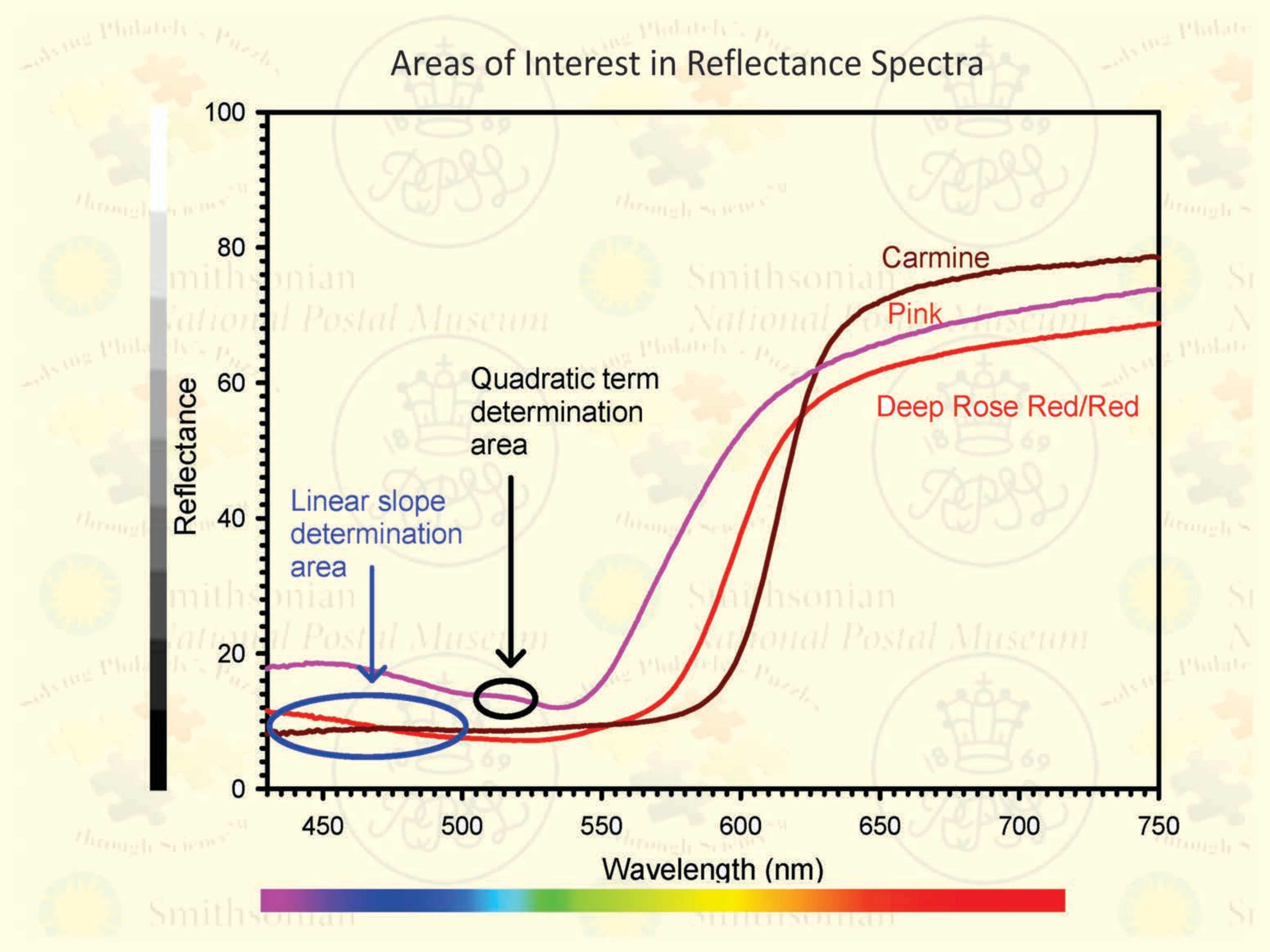
orange
deep orange
brown orange
(3)

Why is There Interest in the 2Ȼ Carmine?

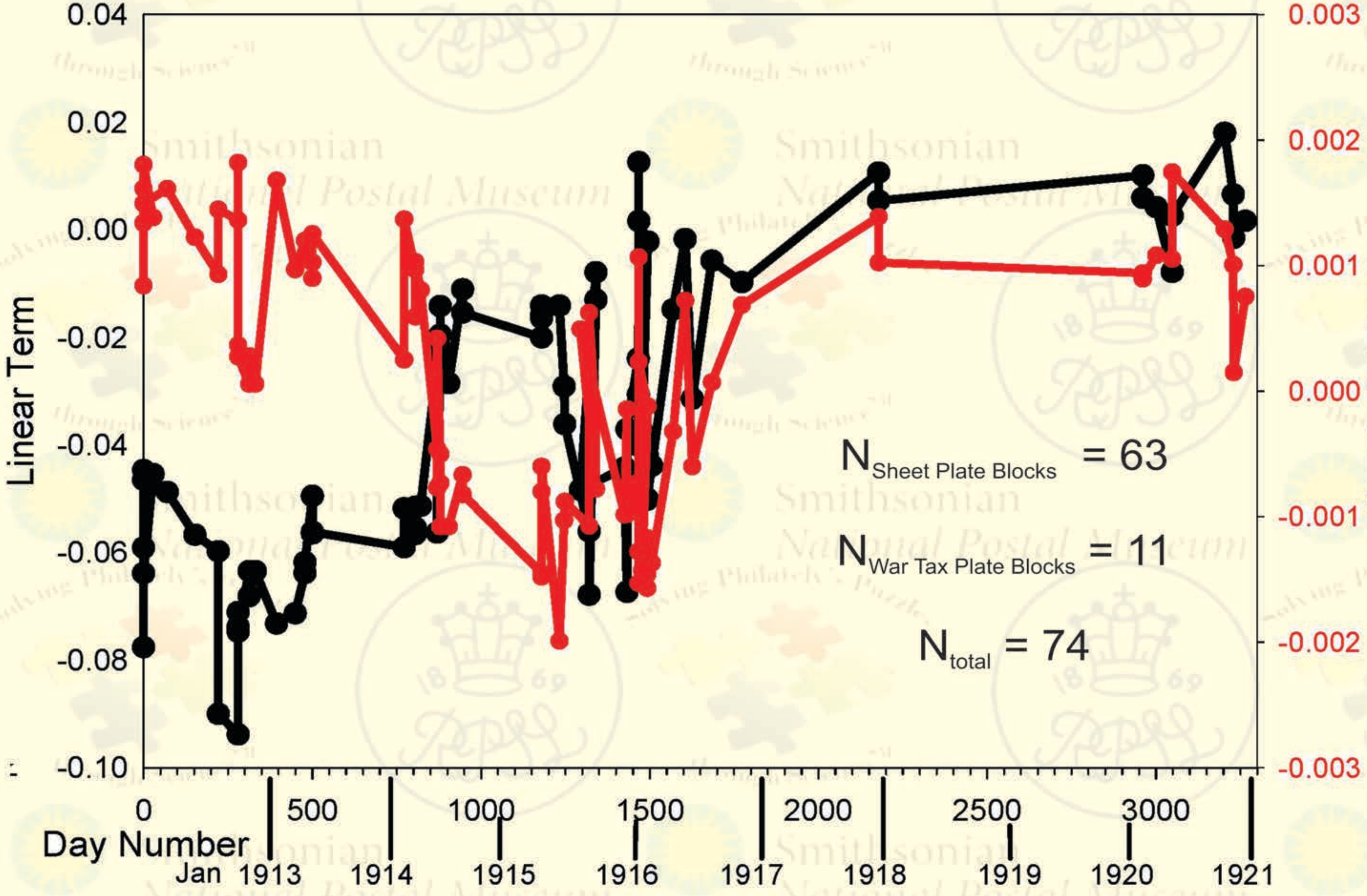
- Largest number of shades with the pink shade at a 5x premium cost.
- Inconsistent shade naming by catalogues and authors.
- Production was pre-, during and post WWI.
- Well known but not catalogued ‘aniline’ ink variety.
- Above reasons suggest changes in ink chemistry during its long production history.

Spectroscopic Techniques Used in This Study

- Reflectance:
  - For shade determination
- X-Ray Fluorescence (XRF):
  - For elemental determination
- Attenuated total internal reflection Fourier transform infrared spectroscopy (FTIR)
  - For molecular compound determination
- Hg-253.7 nm Fluorescence
  - For possible changes in dyes.


Areas of Interest in Reflectance Spectra
Reflectance
100
80
60
40
20
0
Wavelength (nm)
450
500
550
600
650
700
750
Carmine
Pink
Deep Rose Red/Red
Quadratic term determination area
Linear slope determination area

Linear and Quadratic Terms vs Date



Observations from the Reflectance Spectra

- A continuum of shades.

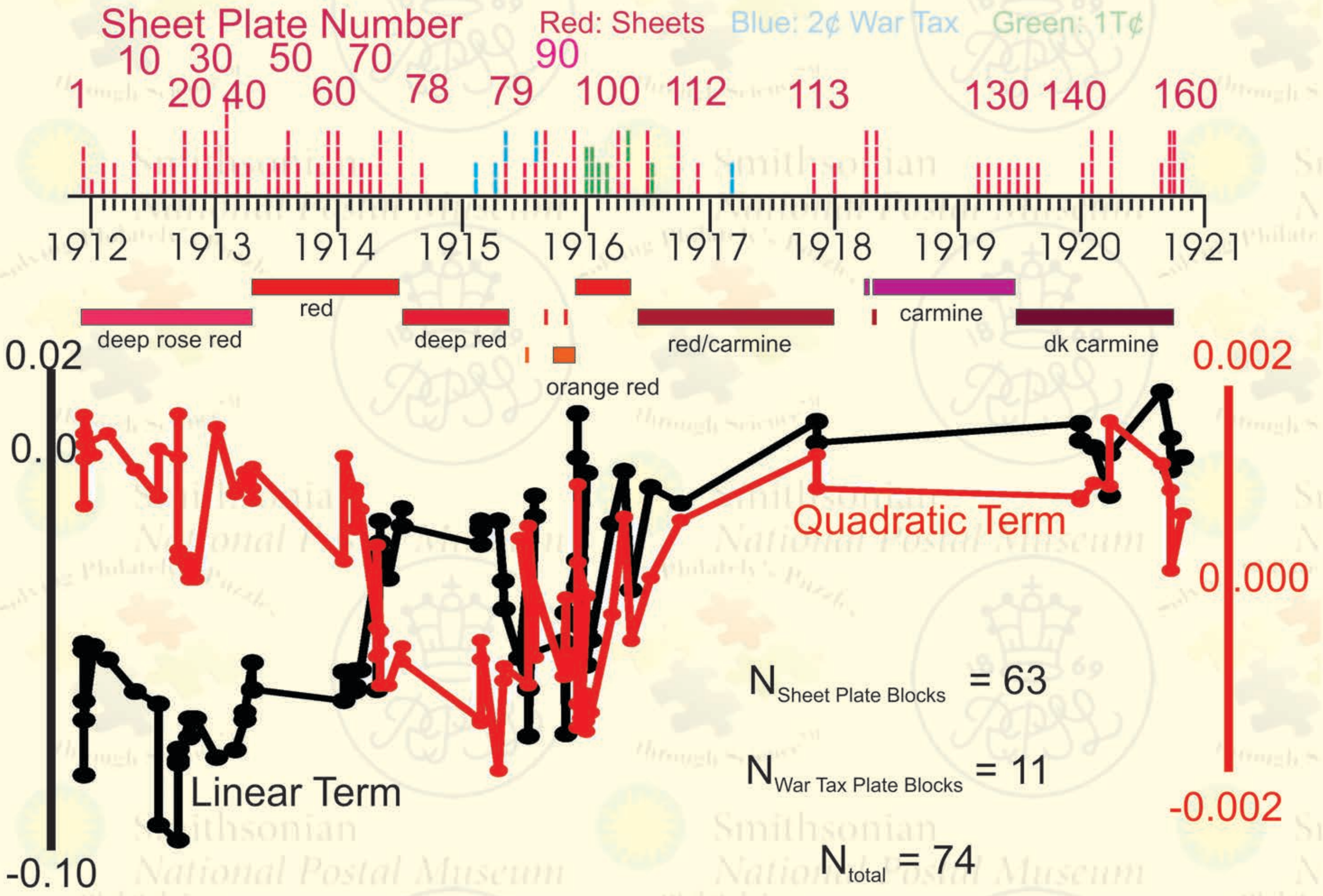
- The linear term show a transition from deep rose red to dark carmine that started around 1914 and was completed by late 1916.

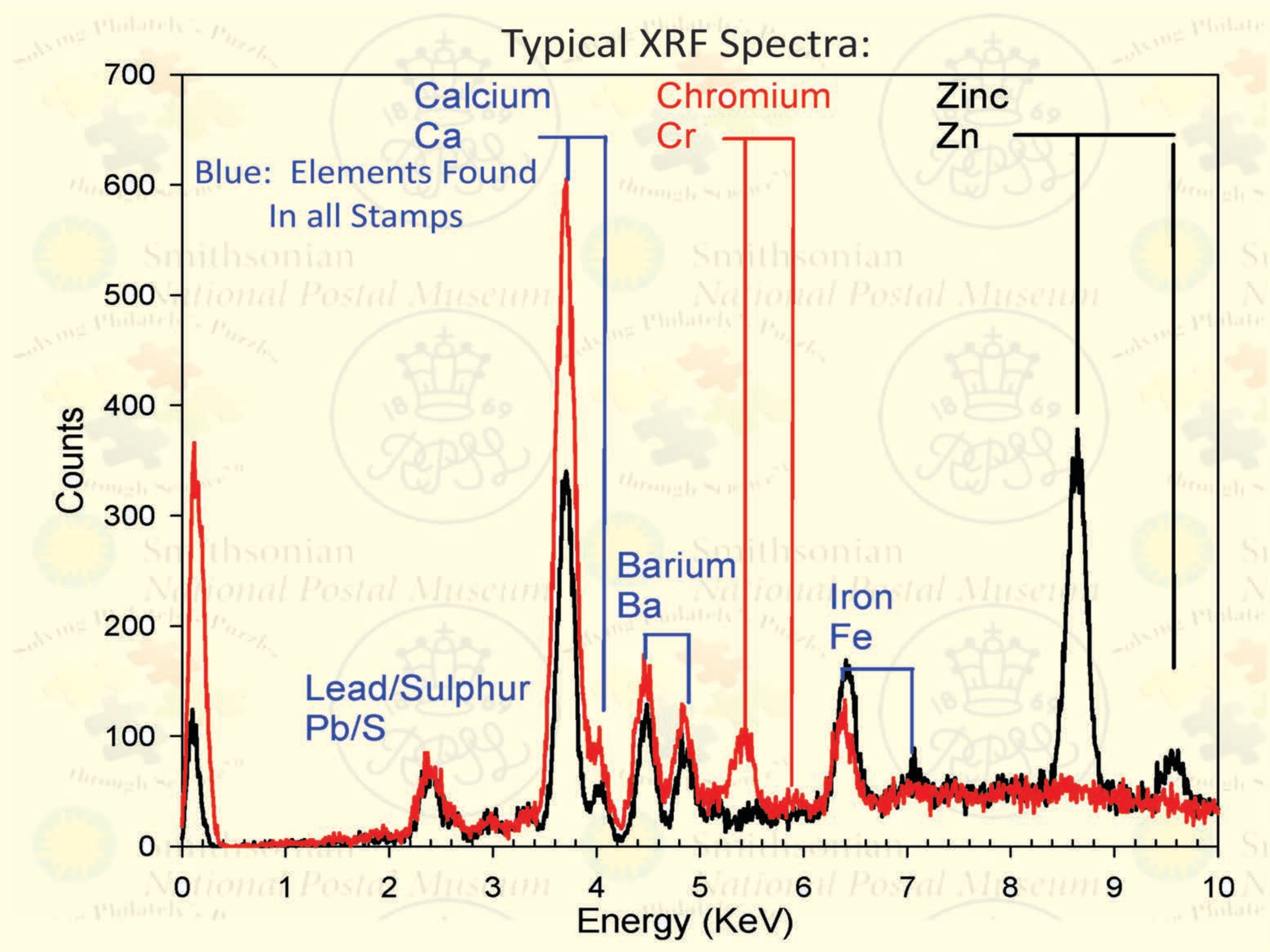
- A negative quadratic term reflects a 'bump' in the spectrum at ~525 nm and appears around 1914 and ends by late 1916.

- Both observations suggest a change in ink chemistry that however can not be confirmed by reflectance spectroscopy alone.

- The reflectance spectra data reflect the philatelist's view of the changes in Admiral shades (next slide).

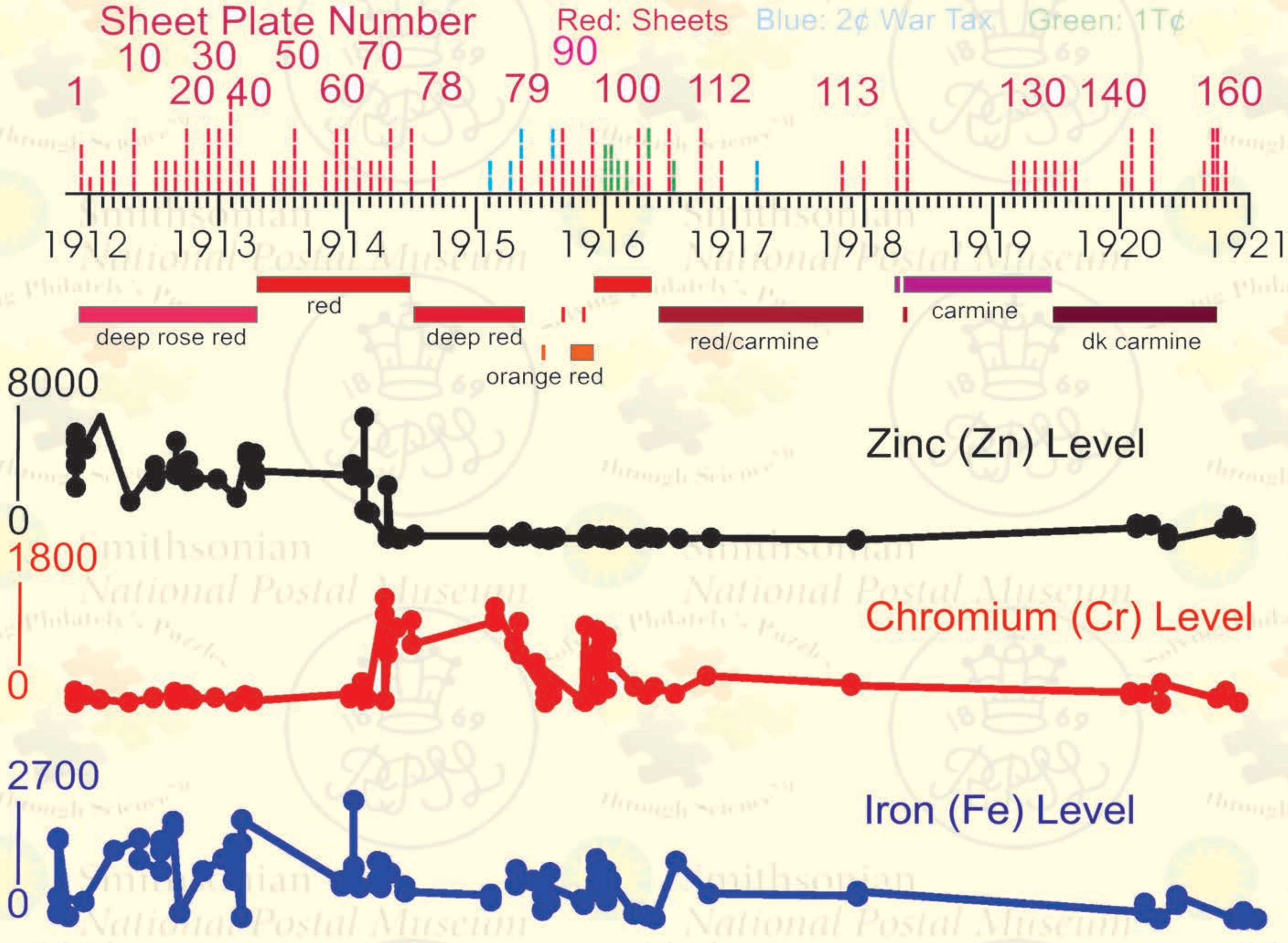
The Unitrade Admiral Shades vs Reflectance Spectra Slopes



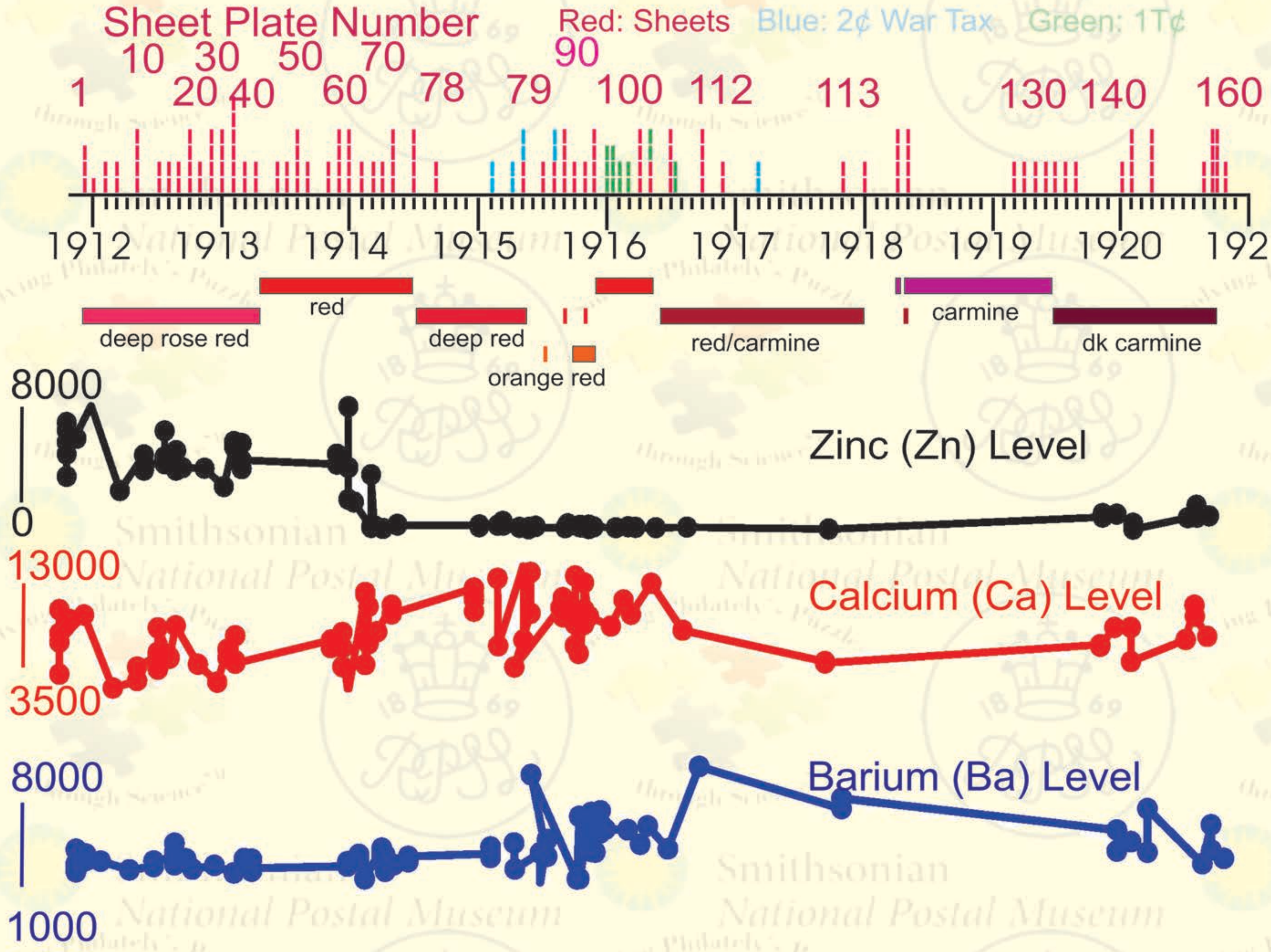


Typical XRF Spectra:
Calcium
Ca
Chromium
Cr
Zinc
Zn
Blue: Elements Found
In all Stamps
Barium
Ba
Iron
Fe
Lead/Sulphur
Pb/S
Counts
Energy (KeV)
0
100
200
300
400
500
600
700
1
2
3
4
5
6
7
8
9
10

Levels of Zinc, Chromium and Iron vs Plate



Calcium and Barium Level Change to Compensate for Loss of Zn



Some Observations from the XRF Data

- Zinc levels are high initially but disappear after 1914. Levels remains below detection limit until minor quantities are seen again near 1920.

- Chromium is absent until 1914. The element appears from 1914 to mid-1916 but levels are erratic. Post mid-1916 levels are low but generally just above detection limit.

- The chromium fluctuations from 1914-1916 parallel the erratic behaviour of the linear and quadratic terms derived from the reflectance spectra.

- Iron is present throughout the period but generally shows a slow decline.

- Levels of calcium and barium are high and increased to compensate for the loss of zinc. Lead levels (not shown) show no trend.

Initial Conclusions from the XRF Data

- Noticeable changes occurred in ink chemistry based on two elements: zinc and chromium.

- Since zinc compounds were used only to dilute the pigment, the shades should not have changed.

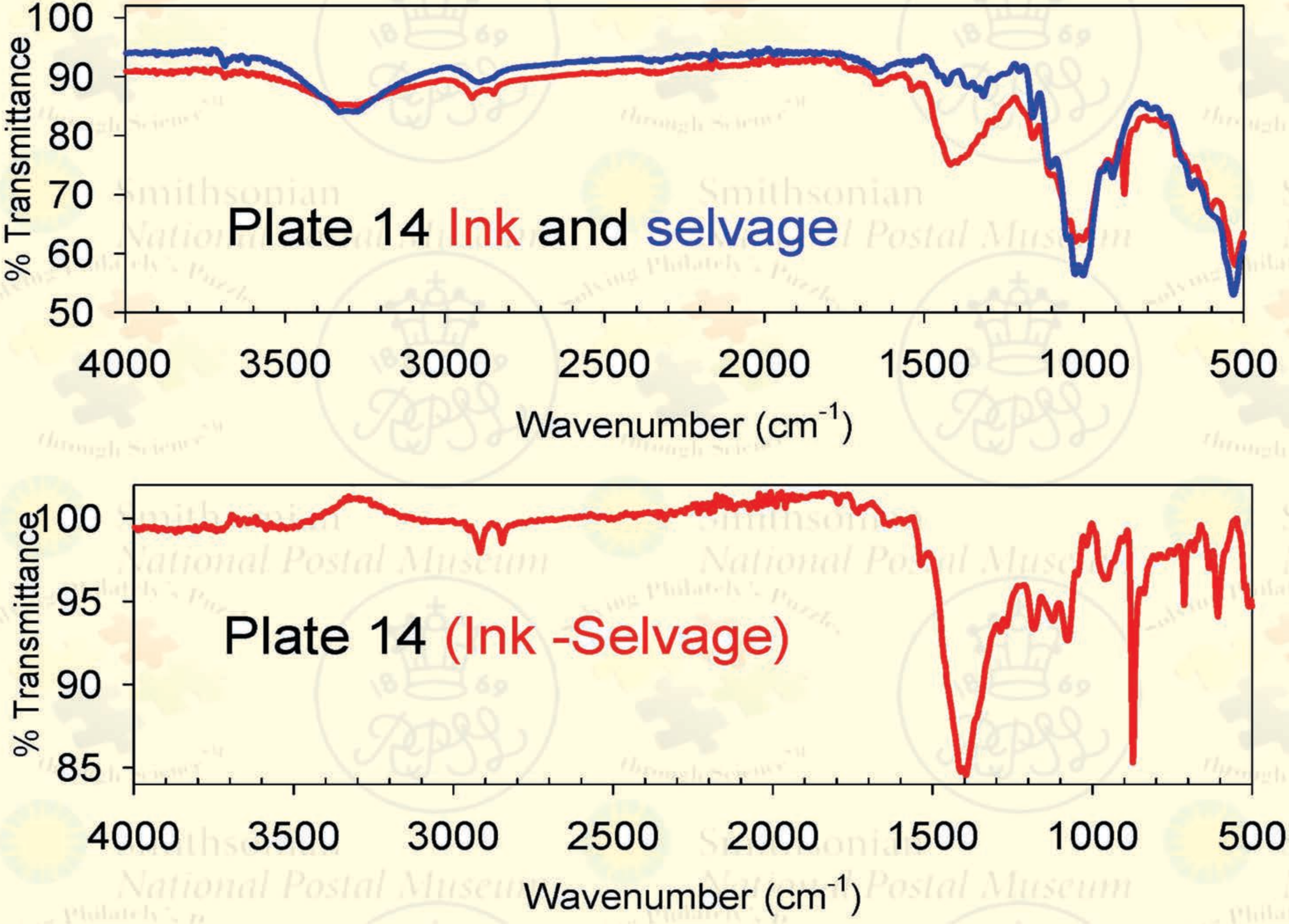
- It is hypothesized that the onset of added chromium and the erratic chromium levels signaled a major change in ink chemistry. This could explain the erratic behaviour of the shades.

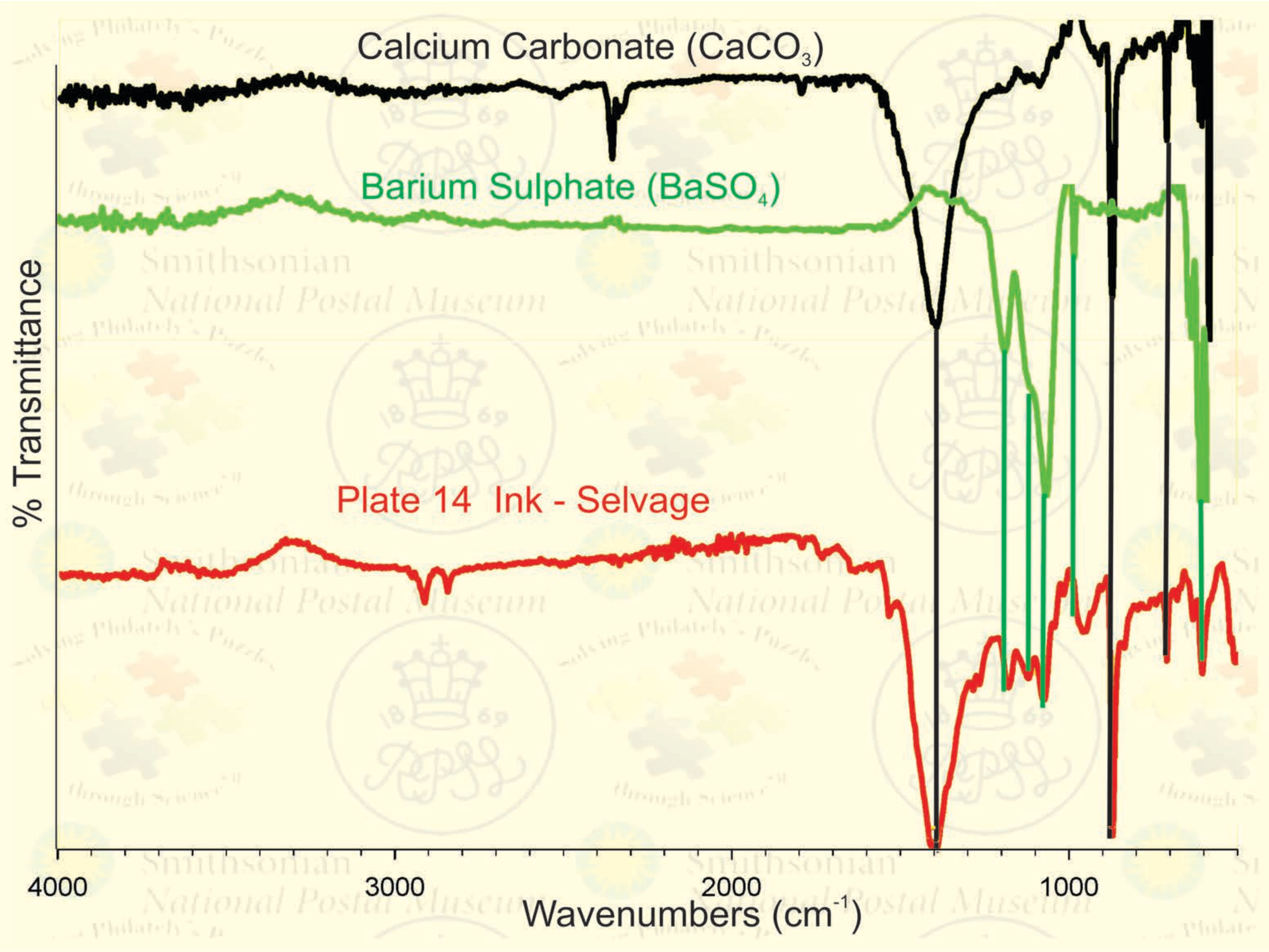
- Was a chromium compound added to modify the shade or does chromium signal a change in dyes used during this period?

- XRF is unable to help here as it can only identify elements present or absent.

- FTIR should help in determining the chemical compounds that remain constant or change during the production period.

Plate 14 FTIR Spectrum Before and After Paper Subtraction





Calcium Carbonate ($CaCO_3$)
Barium Sulphate ($BaSO_4$)
Plate 14 Ink - Selvage
% Transmittance
4000
3000
2000
1000
Wavenumbers (cm^{-1})

Conclusions from the FTIR Spectra (Major Components)

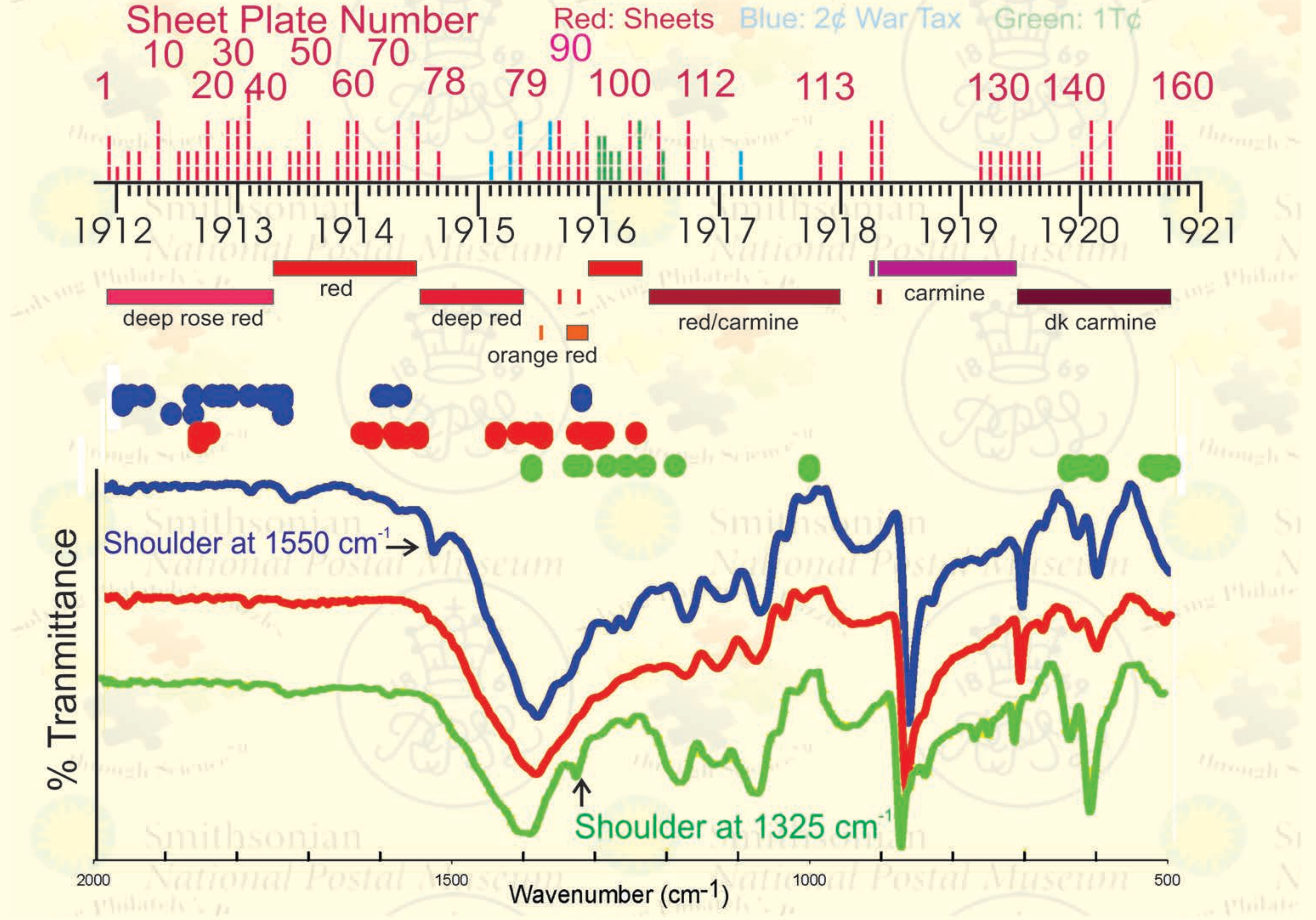
- Both calcium carbonate ($CaCO_3$) and barium sulphate ($BaSO_4$) are present in the ink throughout the production period.

- White lead ($2PbCO_3 \cdot Pb(OH)_2$) is seen as weak peaks at 1045 and 680 cm^{-1}.

- Either zinc sulphide (ZnS) or zinc oxide (ZnO) (or both) are present pre-war but unable to differentiate the two possibilities due to interference from from $BaSO_4$.

- The IR spectra are consistent with lithopone and linseed oil mixture but again not conclusive.

Changing ink chemistry seen through shoulder changes in FTIR spectra



Conclusions from the FTIR Spectra (DYES)

- Disappearance of a shoulder at 1550 cm^{-1} and the appearance of a shoulder at 1325 cm^{-1} parallel the major change in shades (deep rose red/red to carmine/dark carmine).

- A brief time period in mid 1912 and an extended time period from 1914 to mid 1916 had both shoulders missing in a large number of plates.

- This suggests that experimentation with dyes was taking place.

Aniline Ink Definitions (1)

- **The working print shop:**

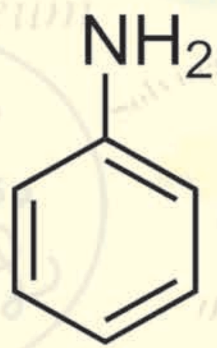
It is usually used in conjunction with aniline printing, now called flexography. It is a printing process that requires a water (or oil) soluble, volatile and a quick drying ink.

- **Commercial dye maker:**

"A fast-drying printing ink that is a solution of a coal-tar dye in an organic solvent or a solution of a pigment in an organic solvent or water".

- **Chemist:**

An aniline ink is formulated from a dye whose complex chemical structure is related to reaction products of starting compounds found in coal tar. Aniline, a major component of coal tar, has a very simple structure.



Aniline Ink Definitions (2)

- **Philatelist:**

"(1) as designating a water-soluble dye in the red color range, usually qualified as 'scarlet' that suffuses the paper and shows through the back to a marked degree, and that, when inspected by ultraviolet rays, fluoresces brilliantly, with a golden or flame color - for example, Great Britain 1912 1d, aniline scarlet; (2) as designating any dye that suffuses the paper and exhibits marked fluorescence when inspected by ultraviolet rays". (Fundamentals of Philately)

Literature References to Plate Number and Aniline Ink

Source	Year	Plate Numbers
Hans Reiche[1]	1965	93-94 (Reworked die group); (pink on back of stamp) (Nov, 1915)
		Unspecified later plates within Retouched Plates (87-90) group; (bright orange red) (Aug to Oct. 1915)
		Unspecified later plates with the Retouched Die (27-86) group. (? to July, 1915)
White, Eaton, Bileske[2]	1969	17 (Vermilion) (Sept, 1912)
		37 (Vermilion) (Feb, 1913)
		81-82 (Vermilion) (June, 1915)
		90 (Orange Vermilion) (Oct, 1915)
		17-94? (Noted as possible) (? to Nov, 1915)
Marler[3]	1982	89-94 (Scarlet-associated with aniline) (Oct to Nov, 1915)
		87-88 (Strong shade of Carmine (aniline?)) (Aug, 1915)

1: Reiche, Hans " Canada The Admiral stamps of 1911-1925", Hans Reiche, [Ottawa] 1965, p 42

2: White, K. Hamilton, Eaton, F.E., Bileski, Kasimir, "Canada Plate Block Catalogue", Kasimir Bileski, Winnipeg. 1969

3: Marler, George C, "The Admiral Issue of Canada" , American Philatelic Society (State College, PA) 1982, p 292

Plate 17 Aniline Ink

- Some plate 17 stamps are known to be the aniline ink variety.
- However, nearby plates also show bleed-through but to varying degrees.
- Do spectra from either XRF or FTIR show major differences in their features?

Plate 17 and Nearby Plates

Gum Side

UV

Plate	14a	14b	17a	17b	18a	18b	19	20	22
Zn	3832	4830	4700	4700	6379	4247	4441	5108	4000
Ca	5189	4121	6050	6311	4998	8226	5962	5852	8384
Ba	2217	1910	2431	2769	2005	3243	2232	2348	1756
Fe	1306	1773	1061	1504	1690	2145	2145	1992	136
Sh @ 1550	YES	YES	WK	YES	NO	SHIFT	WK	YES	YES

Some Observations About Plate 17 Aniline Ink

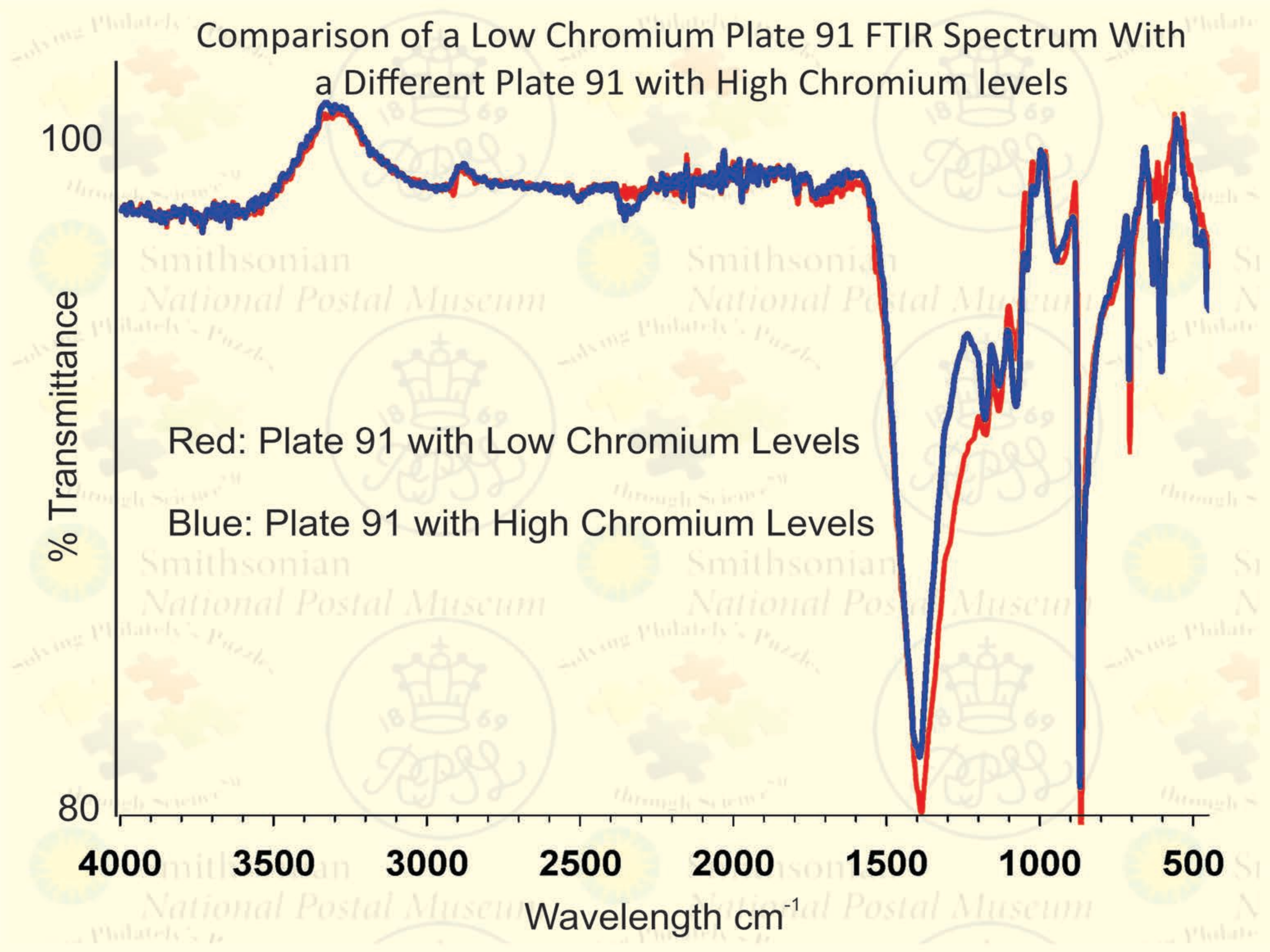
- Except for Fe in plate 20, the count rates for the major elements are similar.
- Bleed through is seen for most stamps but plates 17 (a) and 20 is noticeable.
- There appears to be some experimentation in ink chemistry around plates 17,18 and 19 with the disappearance of the shoulder at 1550 cm^{-1}.
- However, this does not explain the bleed through as plate 20 appears to have the earlier ink chemistry.
- The above suggest that there was some problem with the quality of the pigment around this time frame and some fixes were attempted.

Plates 80 to 94 Aniline Ink

- Plates from around 80 to 95 are the major contributors to the aniline ink population.
- The time period is short from March 1915 to December 1915.

The Major Aniline Ink Period

Plate		UV	Date	Cr	Ca	Ba	Fe
MR2-2			Mar, 1915	1298	9510	2436	403
79			May, 1915	779	6828	1766	1082
81			July, 1915	207	13123	2704	528
82			July, 1915	64	7281	935	198
89			Oct, 1915	96	9787	1194	421
91			Nov, 1915	77	9081	1211	340
91			Nov, 1915	1189	10562	4793	323



Comparison of a Low Chromium Plate 91 FTIR Spectrum With a Different Plate 91 with High Chromium levels
100
80
% Transmittance
Red: Plate 91 with Low Chromium Levels
Blue: Plate 91 with High Chromium Levels
4000
3500
3000
2500
2000
1500
1000
500
Wavelength cm-1

Some Observations for Plates 80 to 94

- Low levels or the absence of chromium (Cr) are seen in the plate blocks with substantial bleed through.

- All other elements are relatively constant

- The fluorescence from 253.7 nm UV light is different for the bleed through plates in that the fluorescence has moved to longer wavelengths.

- No significant difference exists between the FTIR spectrum of low and high Cr plate 91 blocks.

Why Chromium?

- **It could have been used as a shade modifier:**

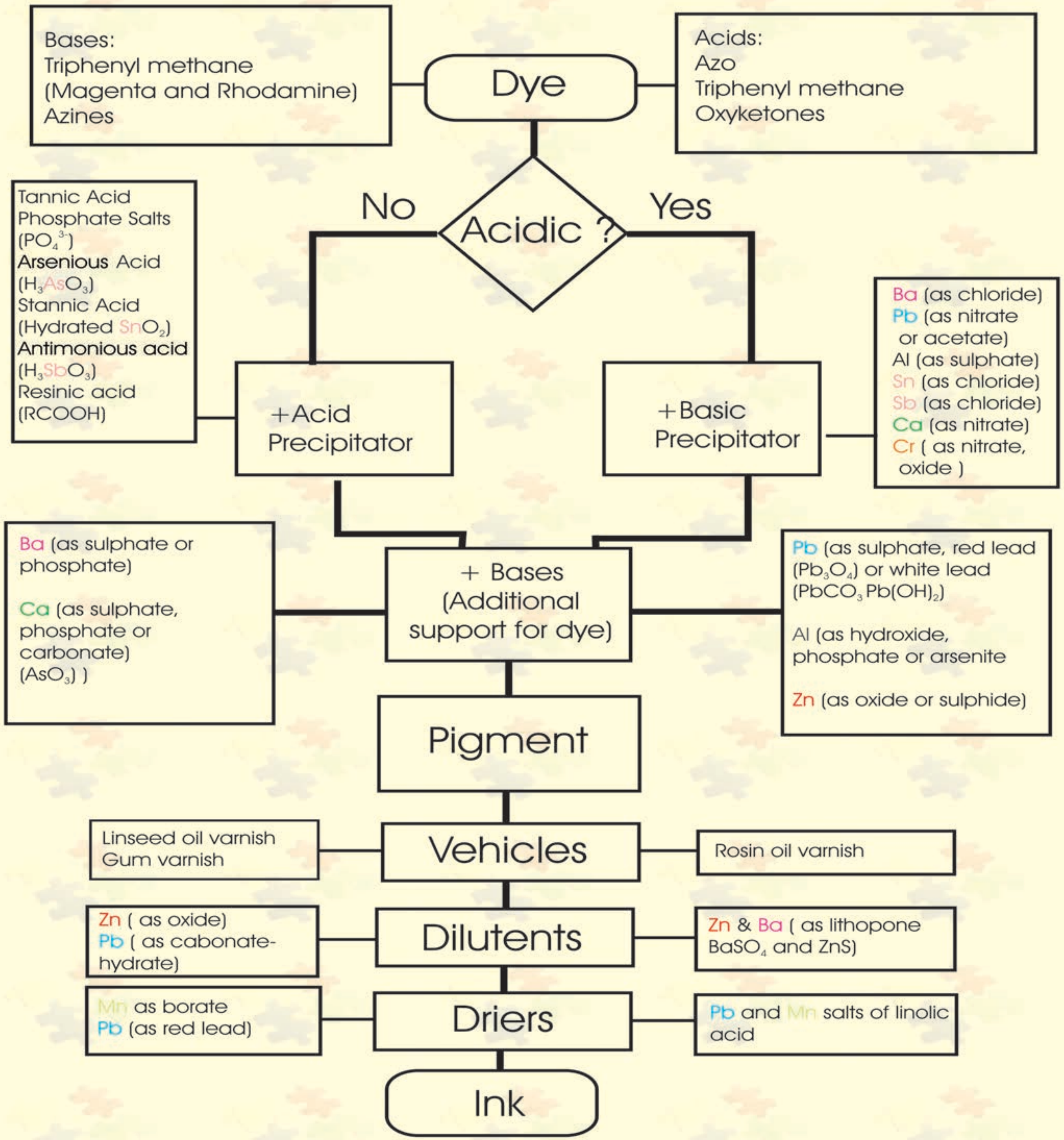
Through the addition of Yellow Orange (lead (II) chromate, $PbCrO_4$) (insoluble) or Yellow Orange in combination with Prussian Blue (an iron cyanide complex, iron(II,III) hexacyanoferrate(II,III)) or Orange Red (the dichromate anion, $Cr_2O_7^{2-}$) (water soluble and unlikely) or even green, insoluble chromium (III) oxide (Cr_2O_3)

- **As a precipitation medium for production of red lakes**

Chromium compound were used in conjunction with calcium oxide to combine with the soluble red dye to form an insoluble solid precipitate which printers gave the term lake pigments or simply, lakes. Chromium (III) oxide is listed in early 1900 literature as one of these agent.

- **Where can Cr enter into the ink making process?**

Flow Chart for Ink Production circa ~1915



Summary Conclusions: Shades

Changes in ink chemistry parallel the shade changes

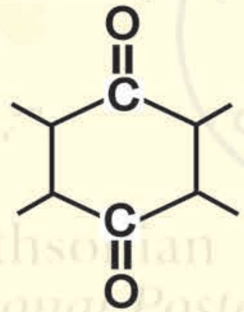
As Seen in the XRF Spectra:

- Loss of zinc (Zn)
- Brief appearance of chromium (Cr).

As Seen in the FTIR Spectra:

- Migration of shoulder peak from 1550 cm^{-1} to 1325 cm^{-1}.

Possibly a change from an azo dye (-N=N–)

to oxy-ketone dyes ()

Summary Conclusions: Aniline Ink

Some bleed through occurs throughout the full printing history.

However the term 'Aniline ink' is reserved for excess bleed though that is seen for only a handful of plates.

For those plates produced during WW I, a weak correlation between low chromium levels and excess bleed though suggests that chromium was used to fix the dye.

Acknowledgments

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