



Using XRD and IR-ATR to Determine Pigment Composition of the US 5-cent 1847 Issue

Gordon Eubanks
Harry Brittain FRSC

2015 IAP International Symposium on Analytical Methods in Philately
Itasca IL 18-19 November 2015

The Stamp

- Issued 1 July 1847
- Five distributions (printings)
- Well over 100 shades recorded
 - 27 major shades from brown to orange
- Original visual study of color
 - by Carol Chase, Calvet Hahn, Roy White and others



Both stamps
unused orig gum

Previous Research

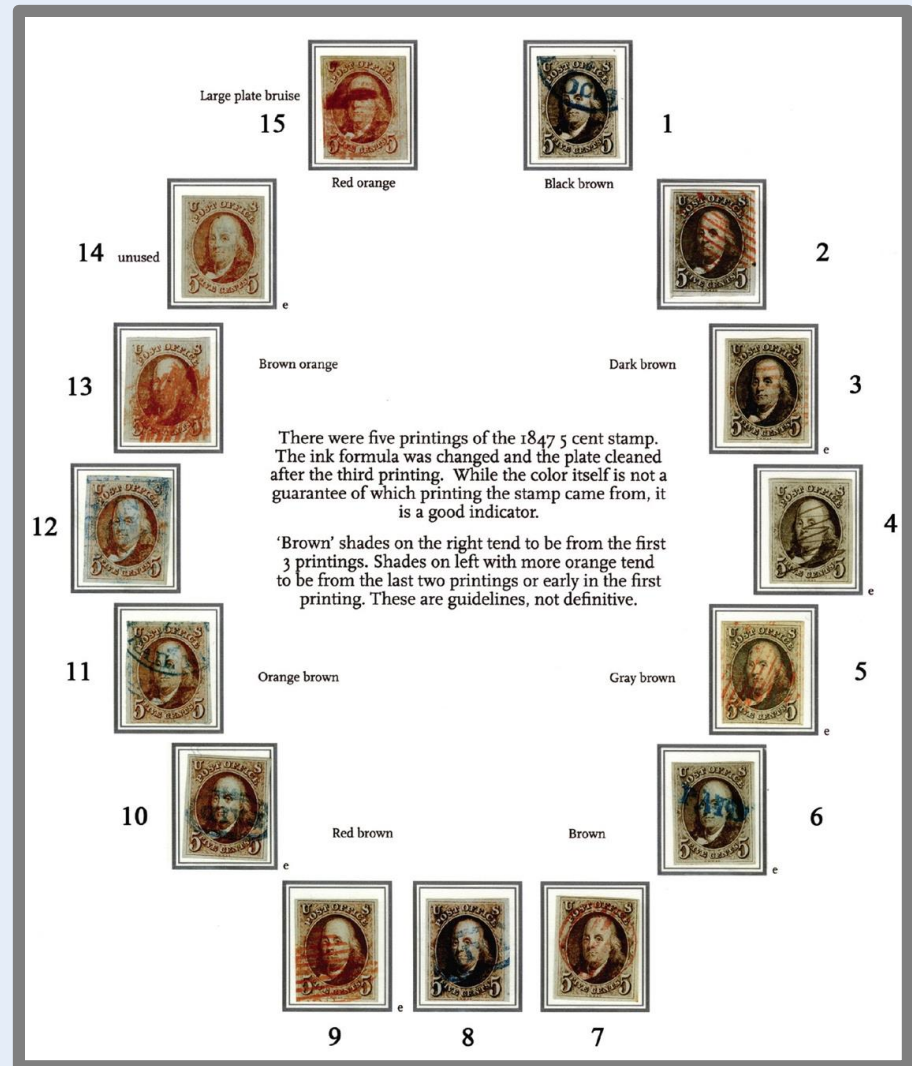
- Visual classification by Carol Chase
 - Studied different shades on existing stamps
 - A few dozen identified
 - Others (Hahn) expanded and improved

Previous Research Part 2

- Visual classification by Carol Chase
 - Studied different shades on existing stamps
 - A few dozen identified
 - Others (Hahn) expanded and improved
- **Wade Saadi Chronicle article August 2013**
 - Used X-ray fluorescence (XRF) to study elements in ink
 - Determined components in the ink are lead based
 - Thus approach used can not determine which compounds of lead are present

Color Wheel

Stamps appear to vary in color from almost orange to dark brown. Same stamps used by Saadi in his research with same ID numbers.

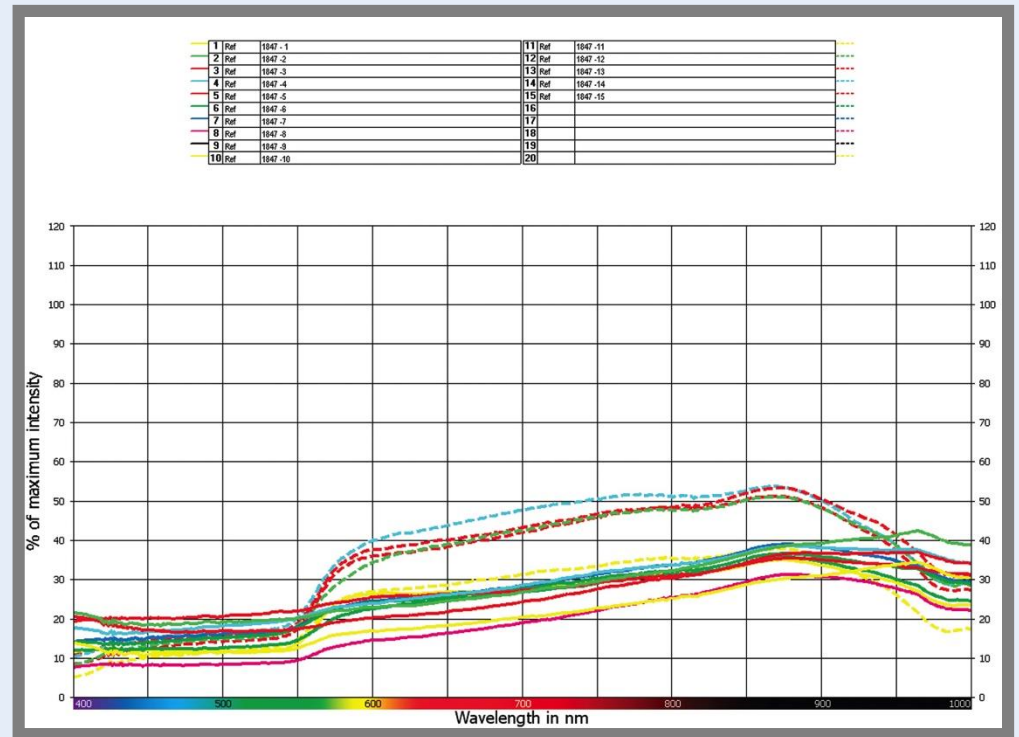


Average Reflectivity Per Shade

Analysis of reflected light to determine color and luminescence of a sample. All samples from the color wheel.

Produced by Tom Lera at the National Postal Museum. Figure 4 in Saadi's Chronicle Article.

Brown oranges and red oranges show greater luminosity.

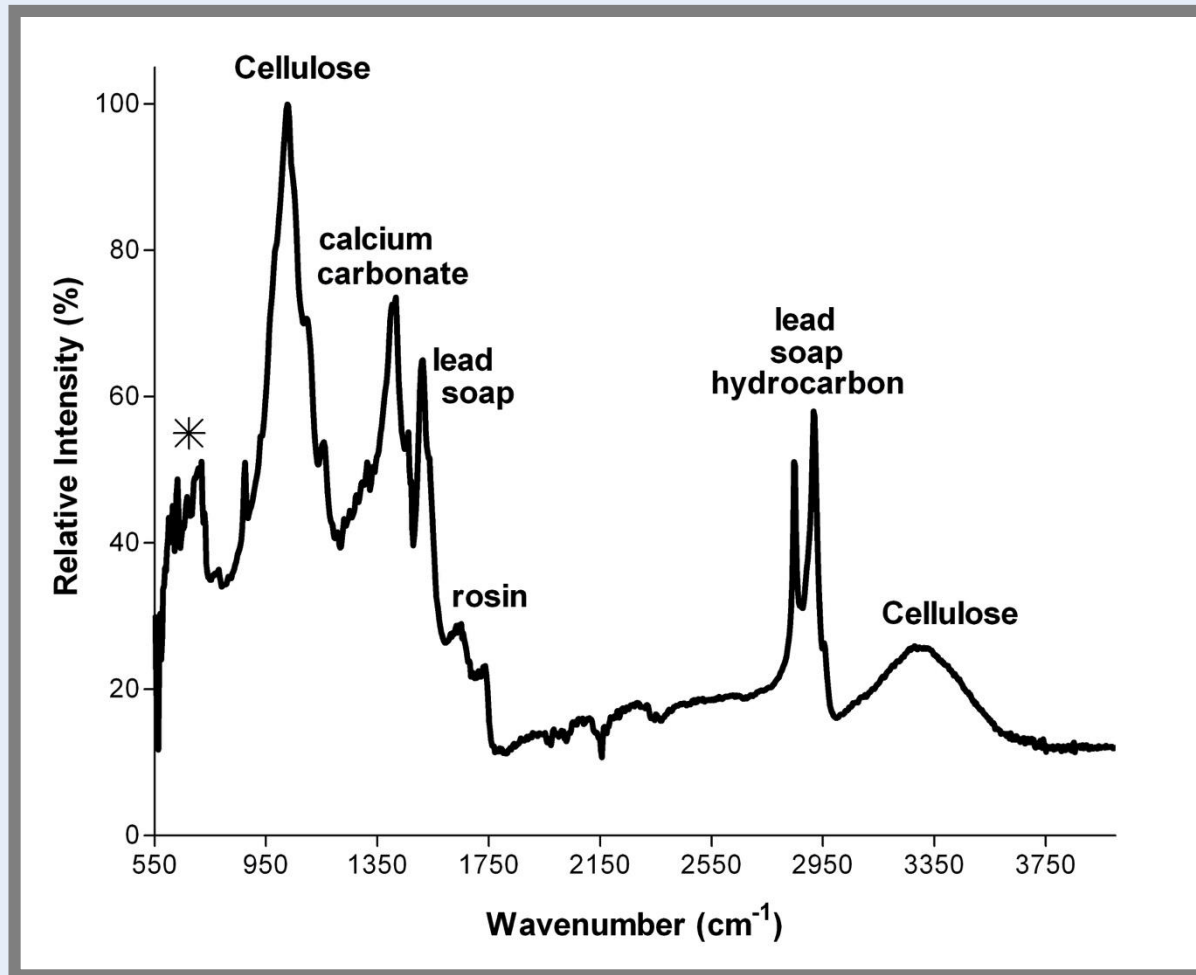


The Goal of this Research

Use X-ray diffraction (**XRD**) and infrared absorption spectroscopy with attenuated total reflectance sampling (**IR-ATR**)
determine the components of the ink
using the same stamps as Saadi.

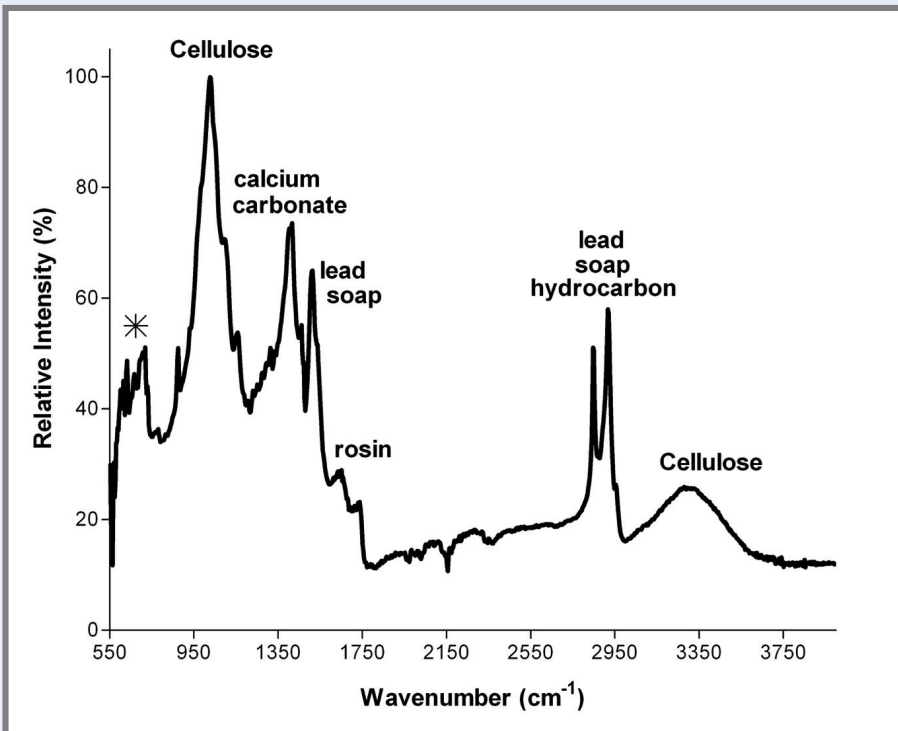
In other words, Saadi determined only lead was present. What are the components of lead?

Infrared Absorption Spectroscopy (IR-ATR)



Average of 15 stamps in color wheel

Infrared Absorption Spectroscopy (IR-ATR)



This is what is in the ink now
Cellulose from paper stamps
printed on

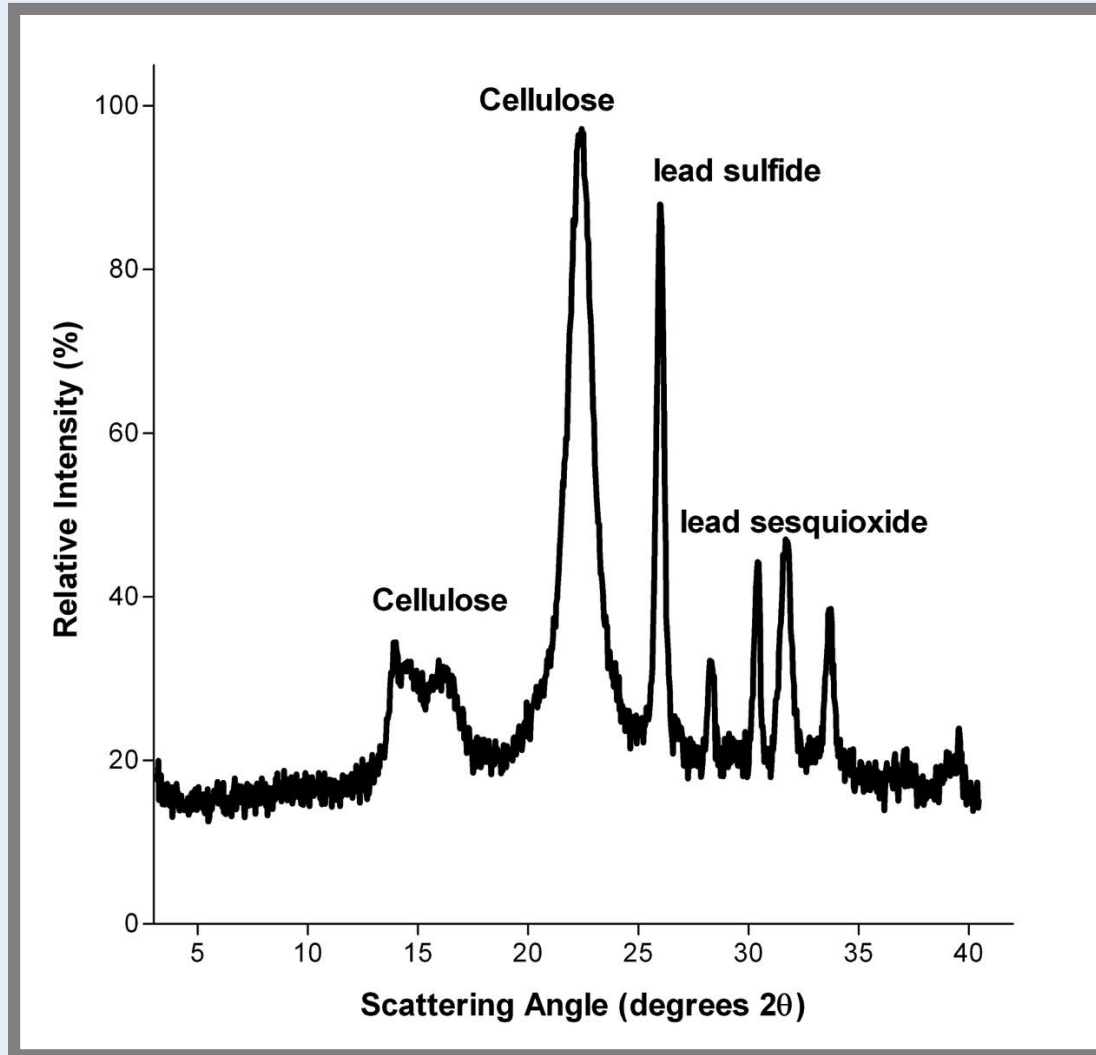
Rosin binds cellulose particles in
the paper

Soap is present

Reaction with lead oxide results in
lead soap

Calcium carbonate is a white
pigment that lightens the black and
extends the ink

X-ray diffraction (XRD)



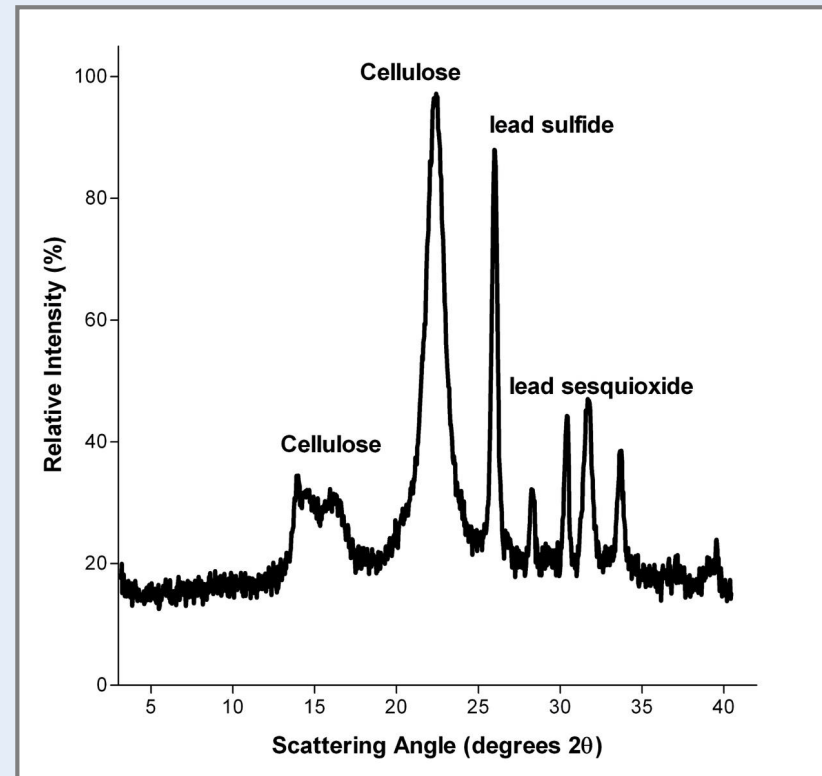
X-ray diffraction (XRD)

Again this is what is
present now

Cellulose from paper
stamps printed on

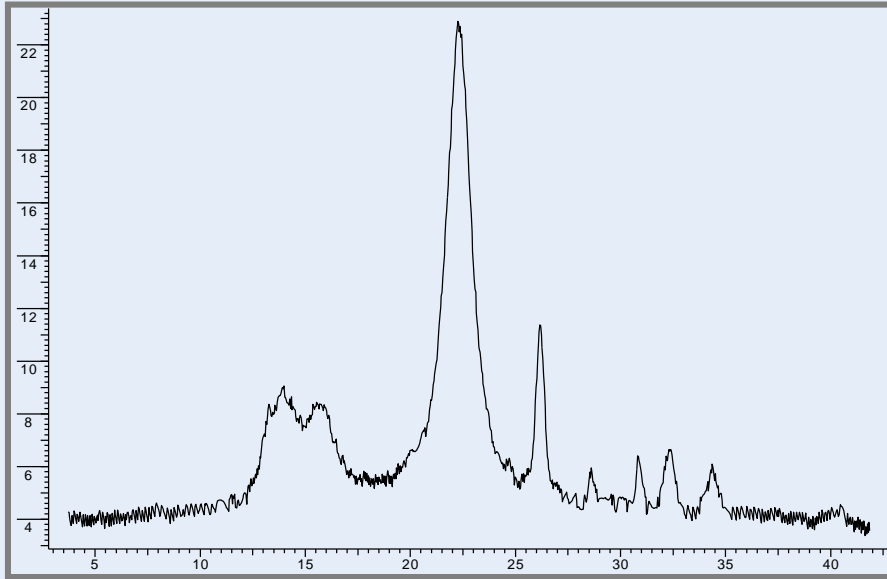
Crystalline Lead sulfide
(PbS) found on stamps

Lead sesquioxide red
pigment

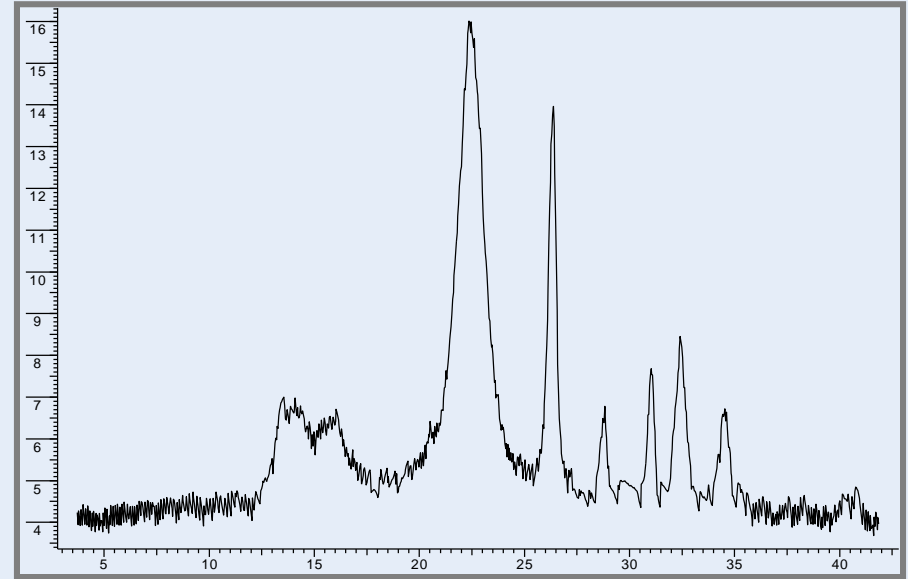




Compare 2 Stamps. XRD Positions L2 & R1



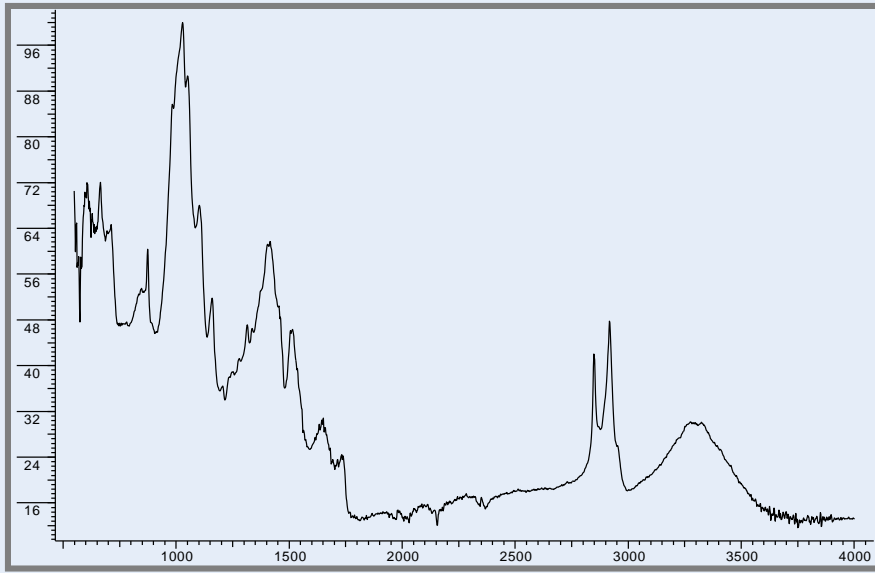
Orange stamp



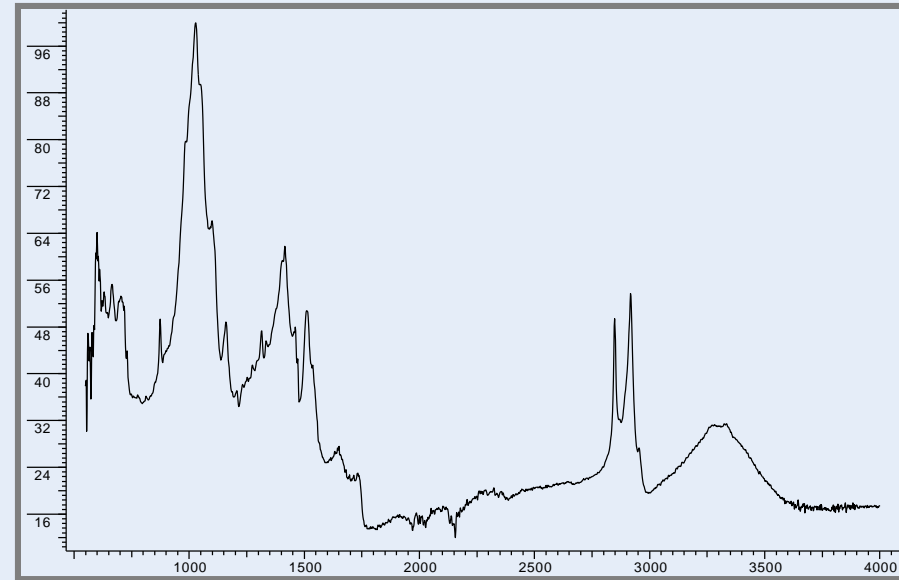
Brown Black stamp



Compare 2 Stamps. IR-ATR Positions L2 & R1



Orange stamp



Brown Black stamp

Issue That Can Affect Color

- Soap is a product of a reaction with red lead and linseed oil.
- Compounds for ink measured in different ratios
- Calcium carbonate reacts with acid in air, paper
- Reds turn orange exposed to moisture and CO₂
 - Van Gough's reds

Issues Affecting Color Not Measured

- Particle size in ink
- Soaking in water with vinegar transforms lead
- Most important what were the original components of the ink!

So What Is the Ink Made Of?

- Eye perception of color is a poor indicator of original ink compounds
- Primary components identified
 - Calcium carbonate (CaCO_3) – white
Finely ground chalk or oyster shells
 - lead sulfide (PbS)– dark gray to black
 - lead sesquioxide (Pb_3O_4) – red lead
Known as minimum
- No Chromium compounds found



Questions?

