Forensic Applications of Raman Micro-Spectroscopy with an Emphasis on In Situ Pigment Identification

Brendan Nytes, Chris Palenik, Skip Palenik, and Bryn Wilke
Microtrace LLC

Overview:

- Raman spectroscopy
- Database
- *In situ* identification of pigments
  - *Printing*
  - *Architectural*
  - *Automotive*

Raman Spectroscopy:

- Advantages:
  - Small analysis volume (confocal)
  - Mapping
  - Depth profiling
  - *In situ* analysis
  - Phase identification
- Disadvantages
  - Fluorescence
  - Strong scatterers can dominate the spectrum

Our Instrument

- Renishaw InVia Raman Microscope
- 2 lasers
  - 785 nm
  - 514 nm

Raman Library:

- IR databases are more prevalent that Raman
- Database:
  - Pigments
  - Dyes
  - Minerals
  - Chemical compounds

- Includes over 200 pigments
  - Of ~500 pigments and 2000+ dyes in our physical reference collection
- Can be searched
  - Background/baseline corrections can interfere with search

Pigmented Printing Inks:

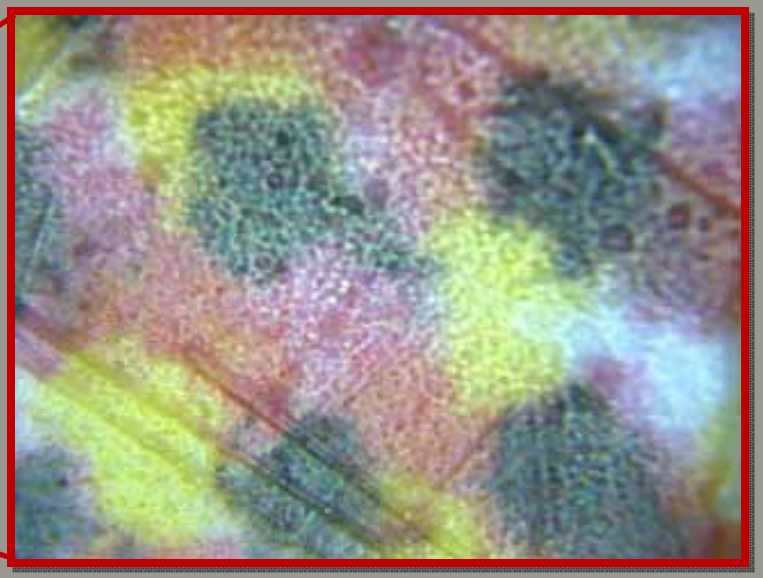
- Starting point
- 4-color process printing
  - Packaging
  - Letterheads
  - Laser printers
  - Commercial printing
- Samples are readily available
- Can study both individual pigments and mixtures produced in the printing process

CMYK Printing Process:

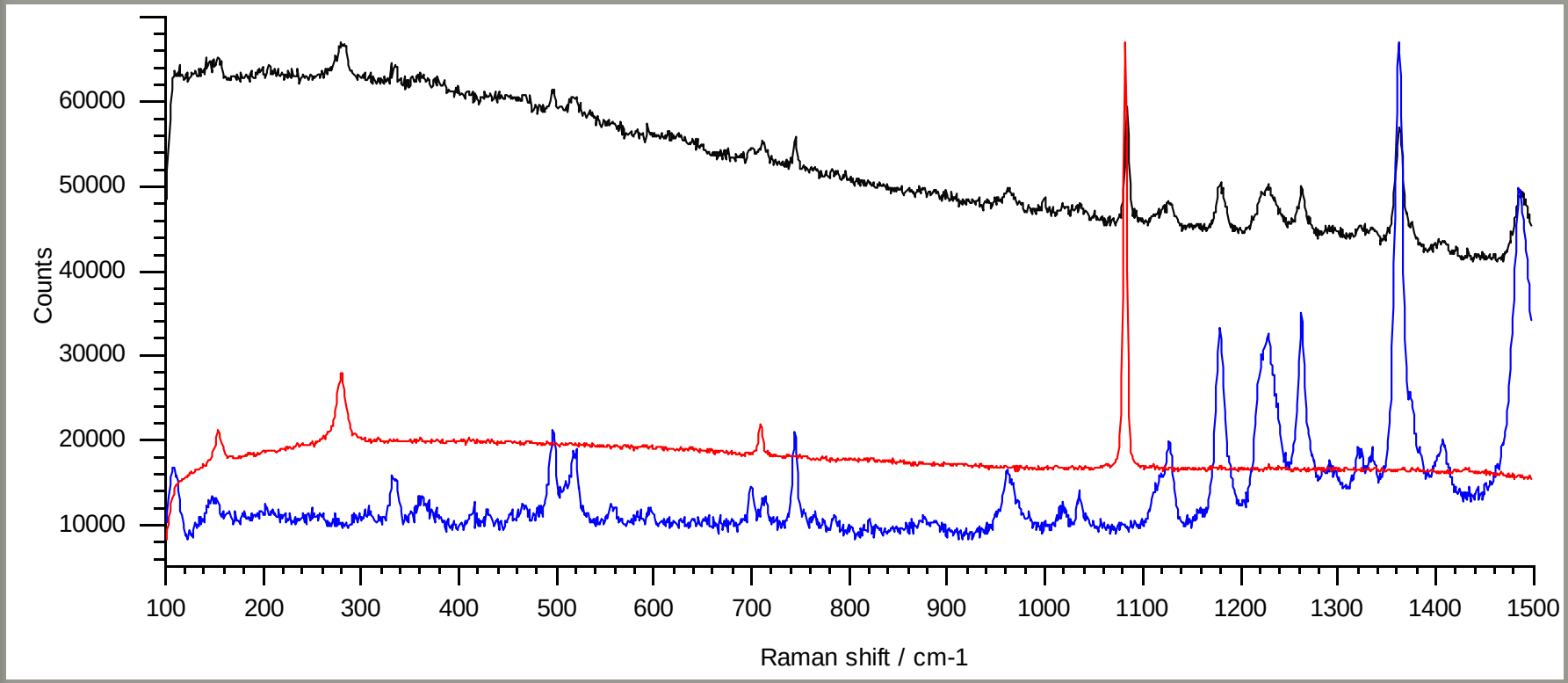
- Primary colors
  - Cyan
  - Magenta
  - Yellow
  - **(K)** Black

- Applied separately and registered
- Overlapping spots of different sizes are used to form a range of composite colors
  - e.g. yellow and blue to make green

Printing Inks:

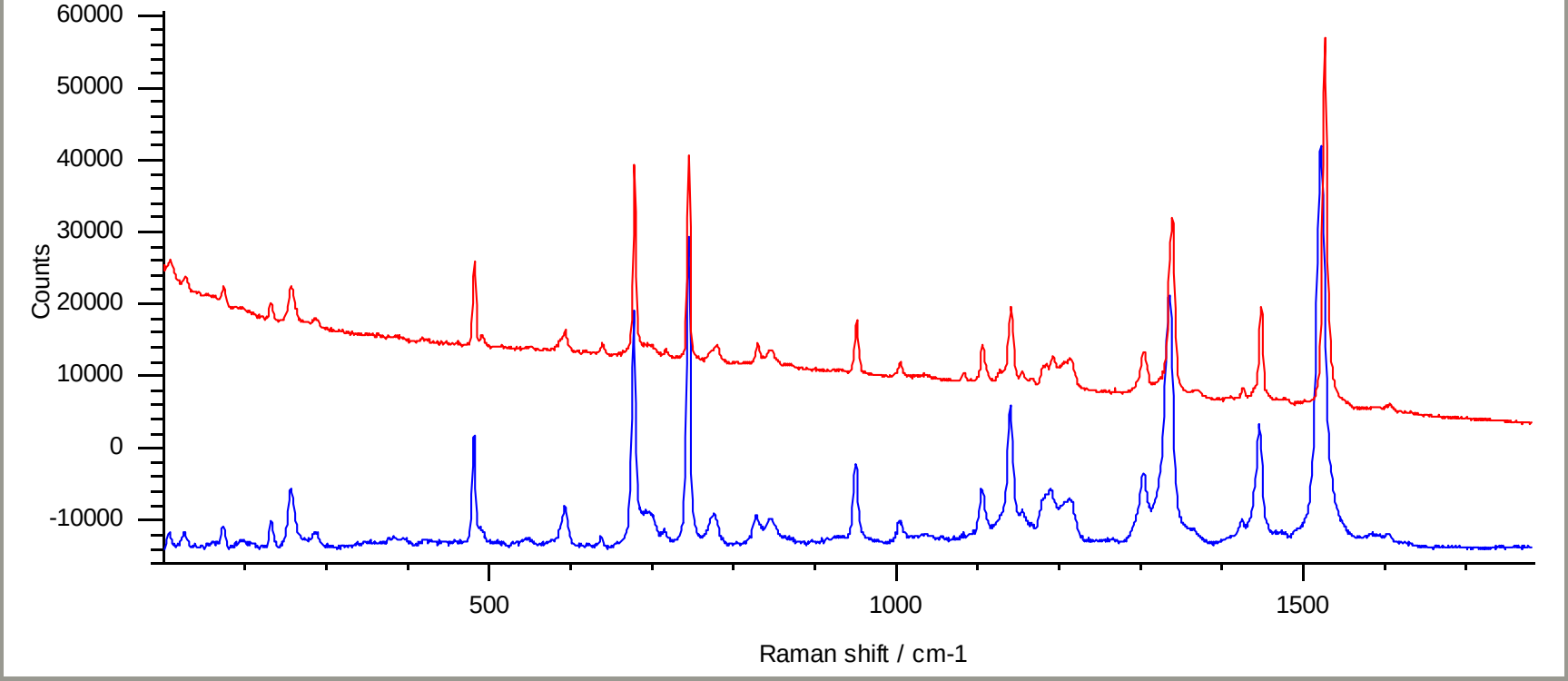


Identification of Pigments
Red Ink: Identified as PR 57



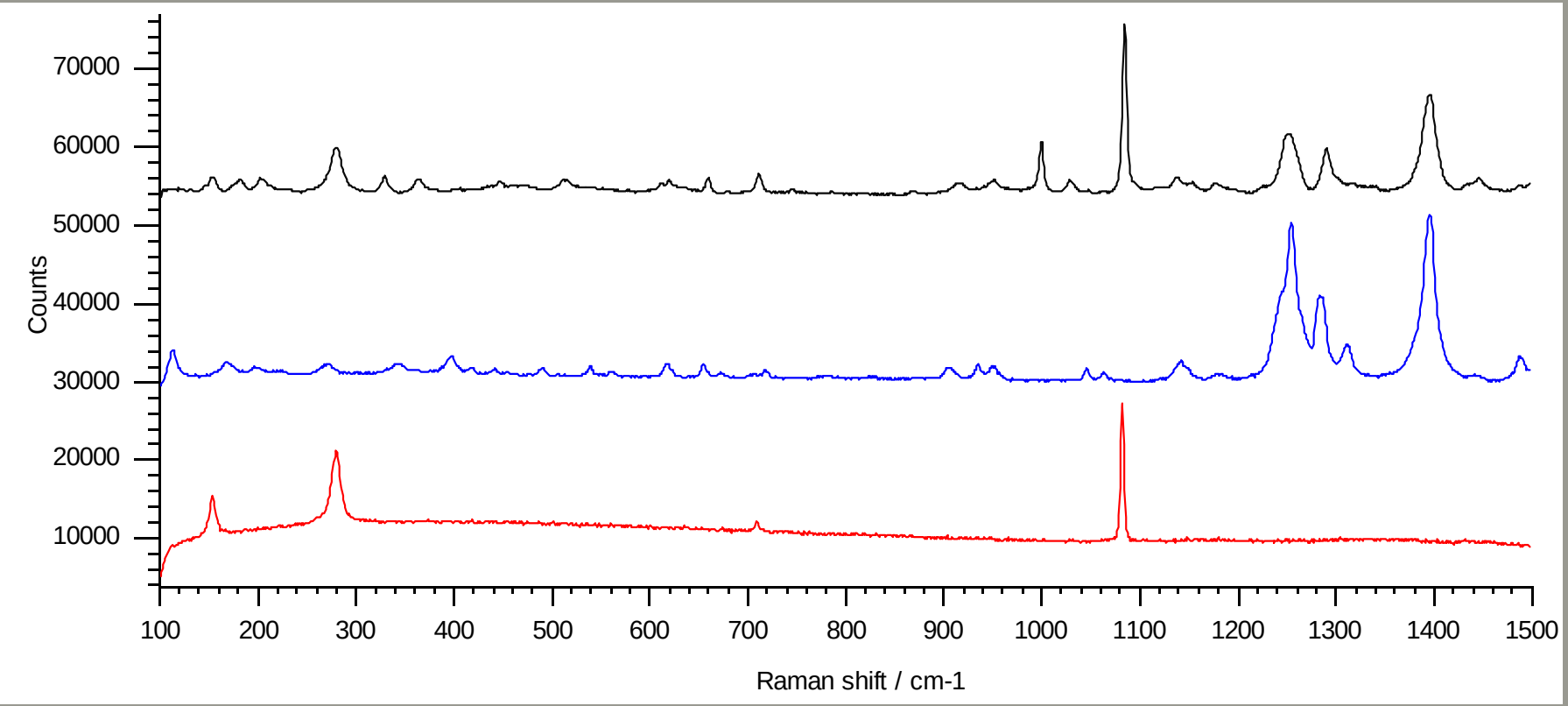
- Black = Red Ink; Red = calcite; Blue = PR 57

Identification of Pigments
Blue Ink: PB15:3/4



- Blue= Blue Ink; Red = PB15:3 reference spectrum

Identification of Pigments
Yellow: PY 12/13



- Black = Yellow Ink; Red = calcite; Blue = PY 12/13

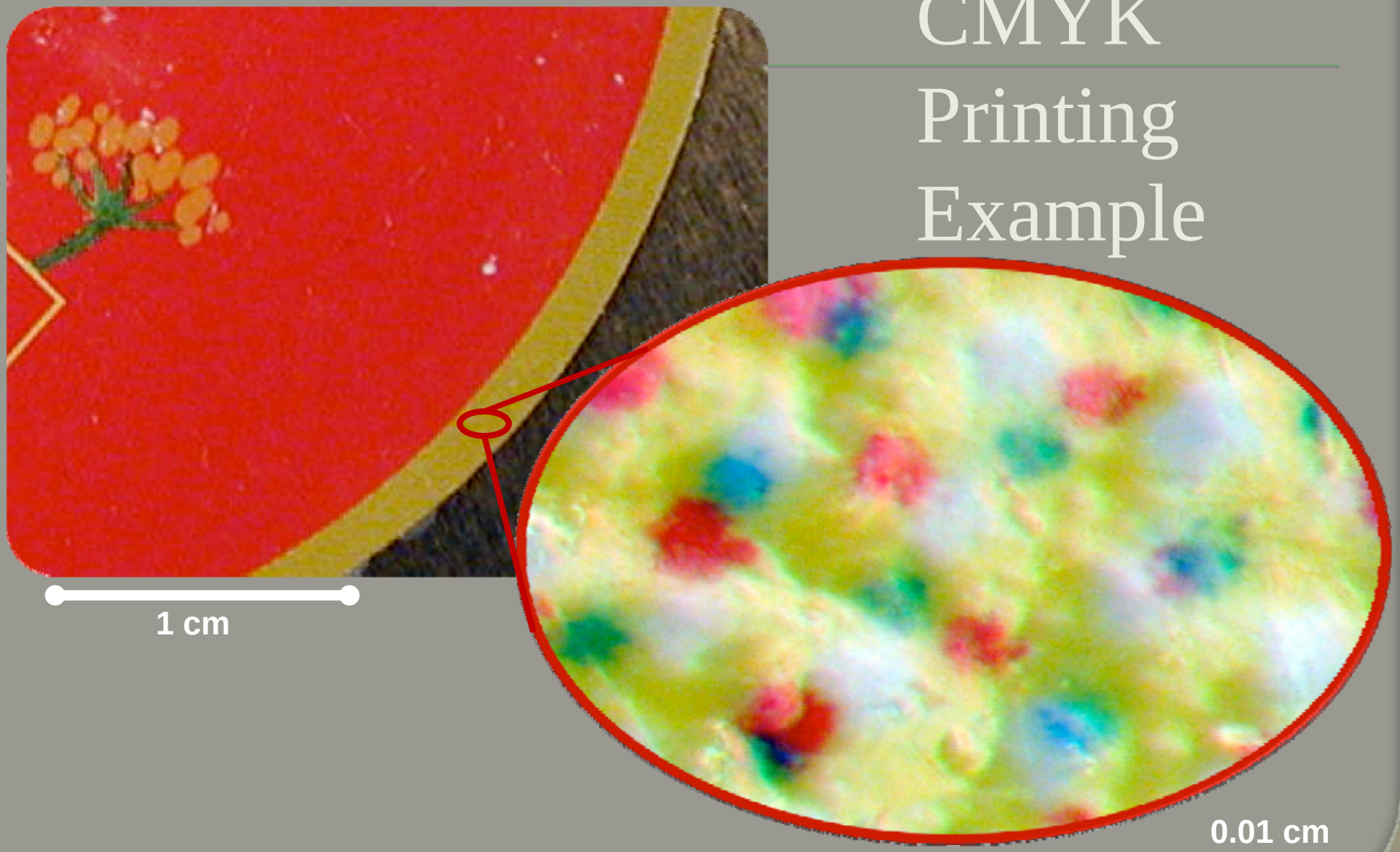
Standardization of CMKY Pigments:

Inks are produced with a single pigment for simplicity, cost, and standardization.

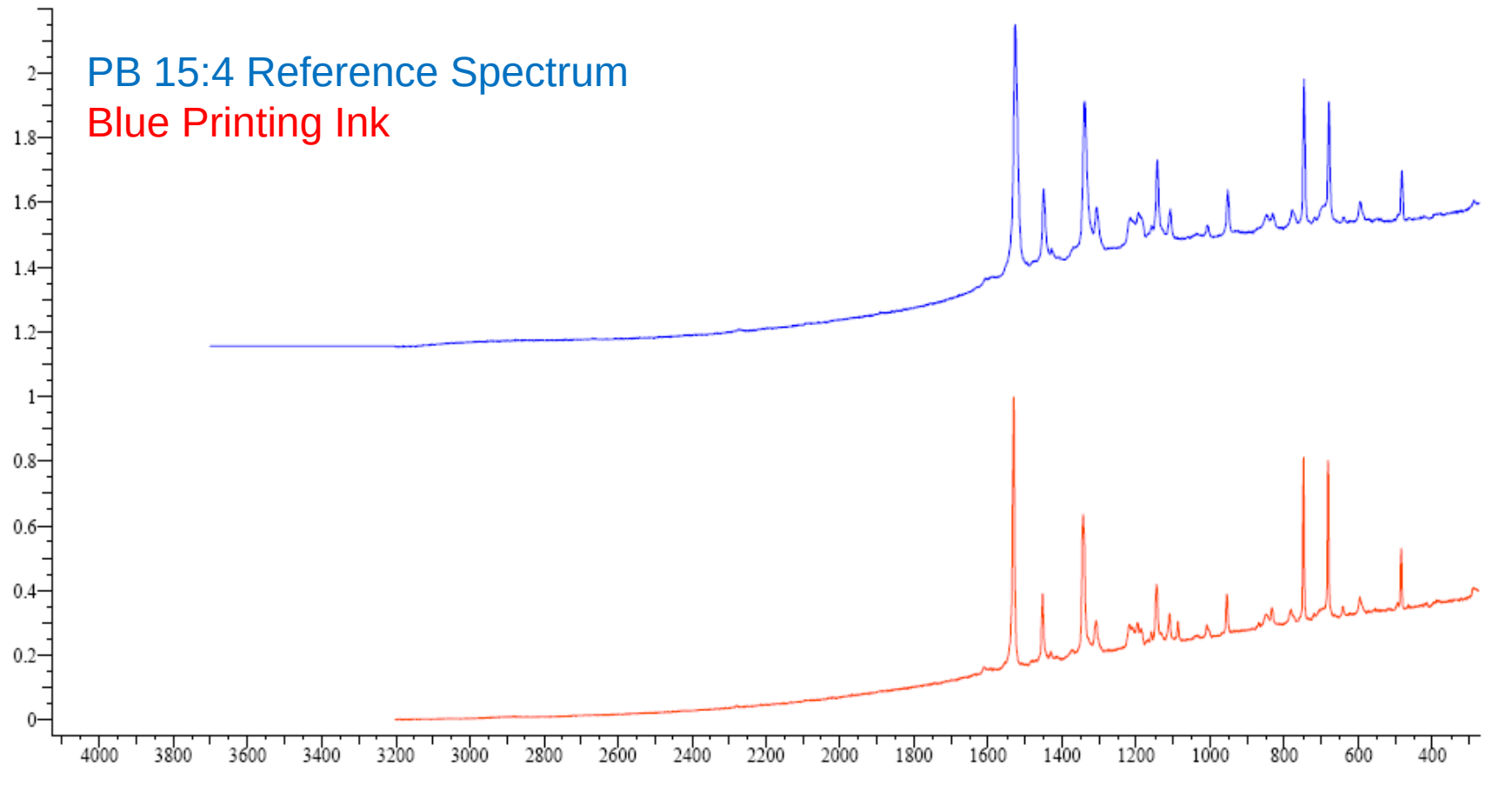
Typical Pigments

- **Yellow:** Diarylide Yellow AAA (PY 12)
- **Magenta:** Lithol Rubine (PR 57:1)
- **Cyan:** Phthalocyanine Blue GS (PB 15:3)
- **Black:** Carbon Black

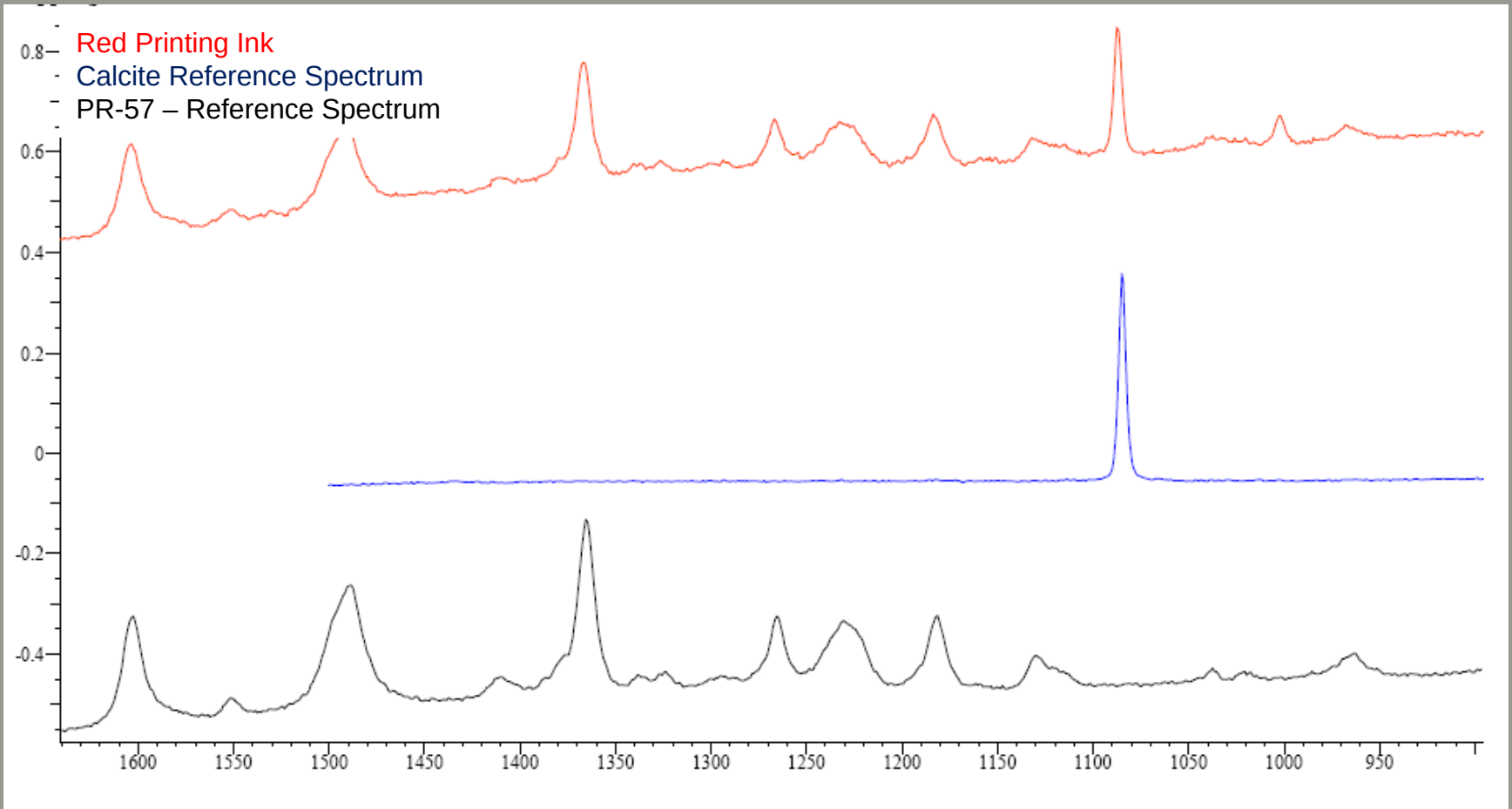
CMYK Printing Example



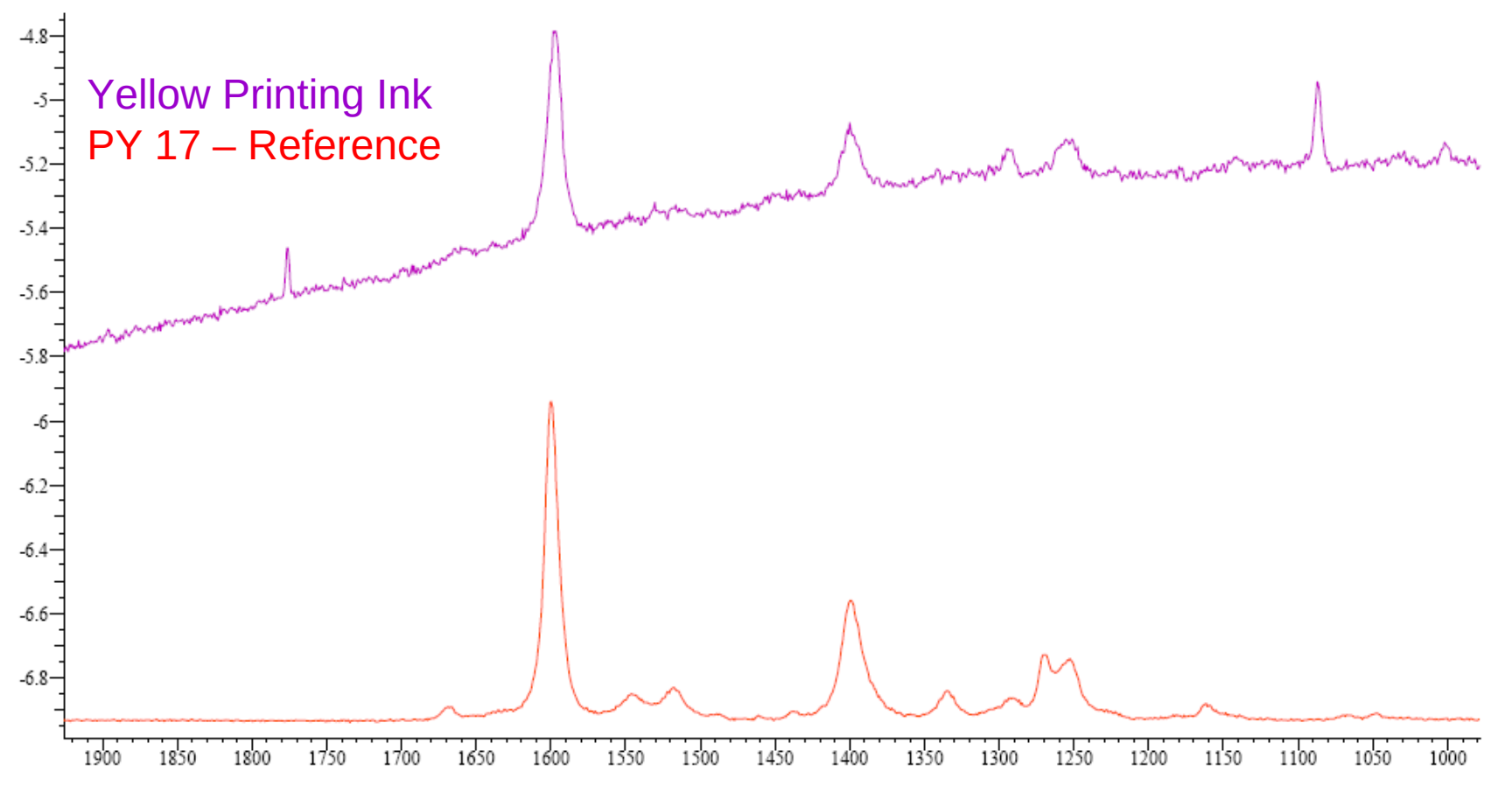
Identification of Pigments
Blue: PB 15:3/4



Identification of Pigments
Red: PR 57

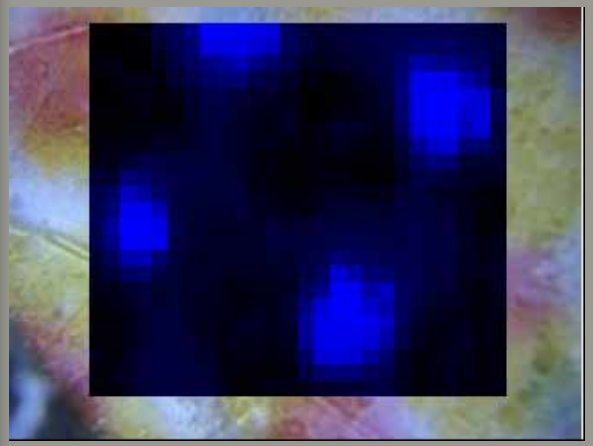


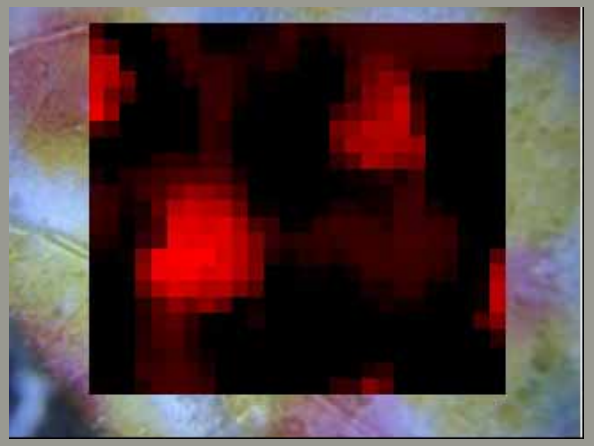
Identification of Pigments
Yellow: **PY 17**

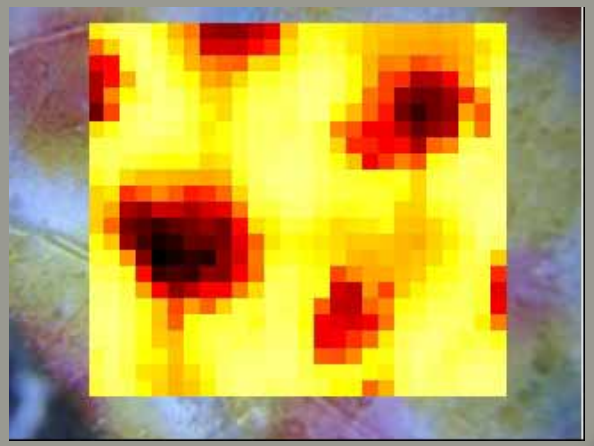


Raman Component Maps:

- Red: PR 57
- Yellow: PY 17
- Blue: PB 15:4







Printing Pigment Wrap-up:

- Multiple pigments were identified
- Pigments were indentified *in situ*
  - No sample preparation

Architectural Paints:

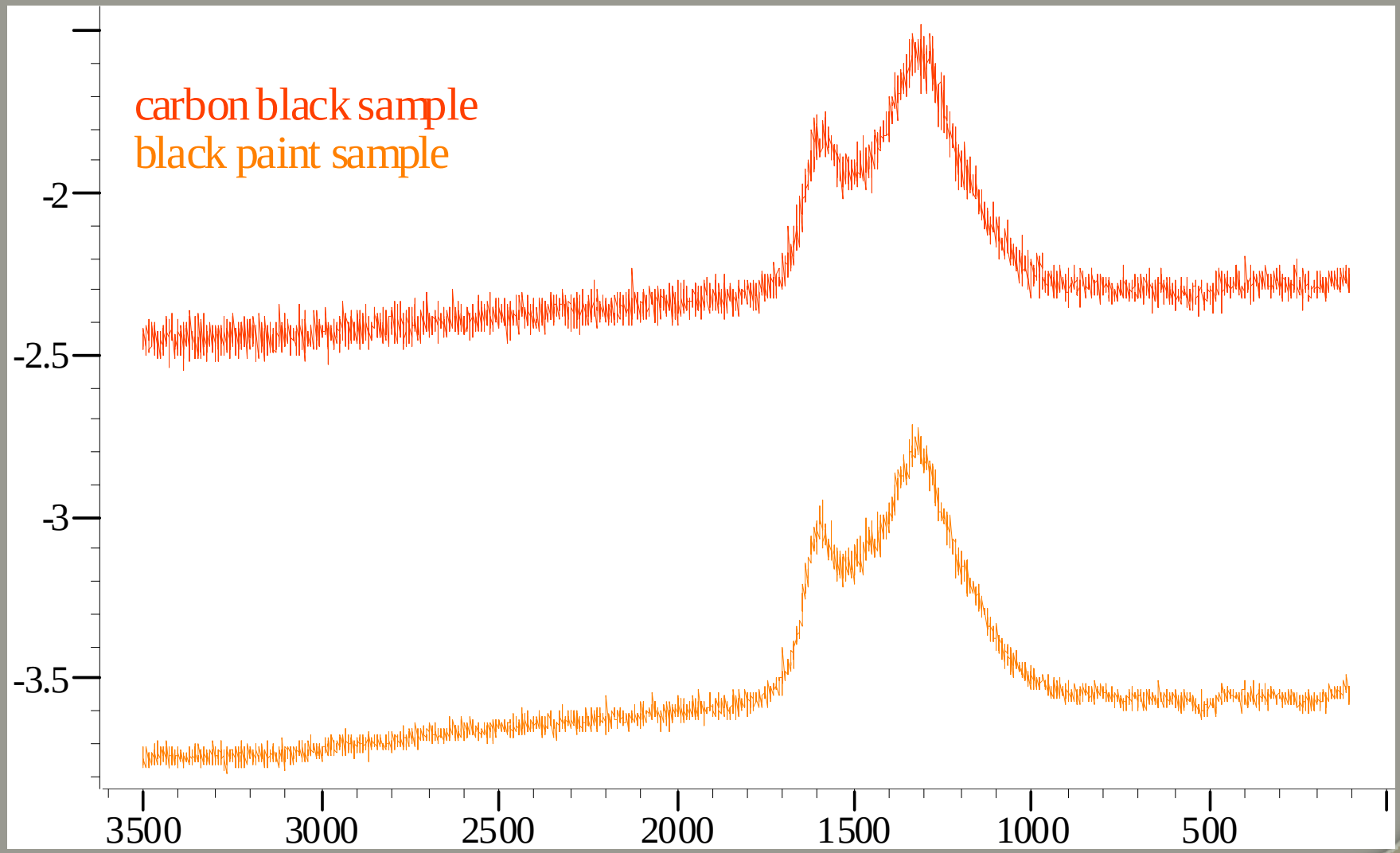
- Encountered in casework
- Limited number of pigments used
- Readily available samples
- Some pigments are listed on the containers
- Seven paint samples

Glidden® Latex Gloss Enamel

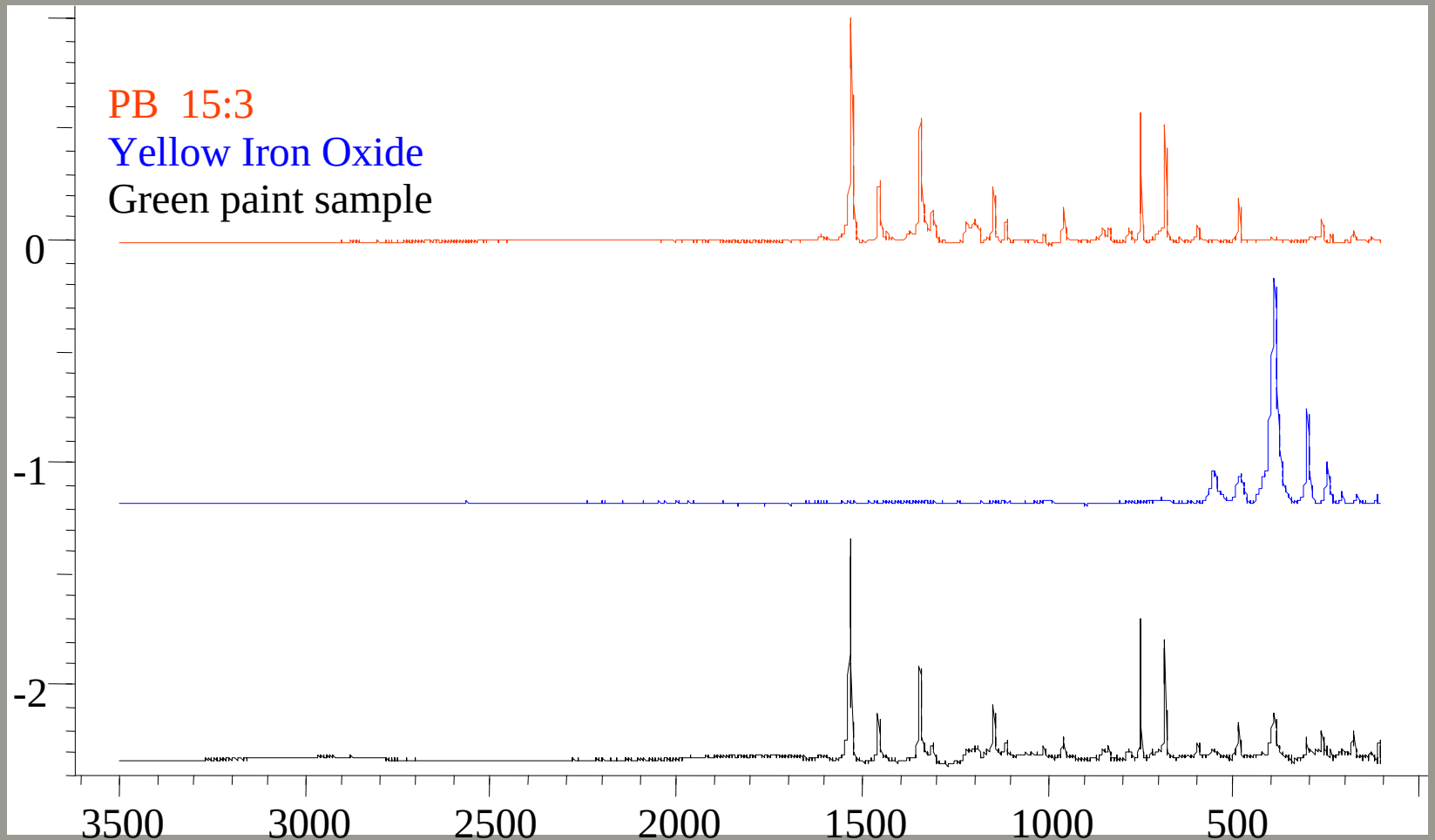
Ingredients Listed on Paint Can:

- Black paint
  - Carbon black
- Gray paint
  - PG 7, Titanium Dioxide
- Red paint
  - PR 3
- Blue paint
  - Titanium dioxide
- Green paint
  - PY 42 (iron (III) oxide)
- White paint
  - Aluminum sodium salt, quartz, titanium dioxide

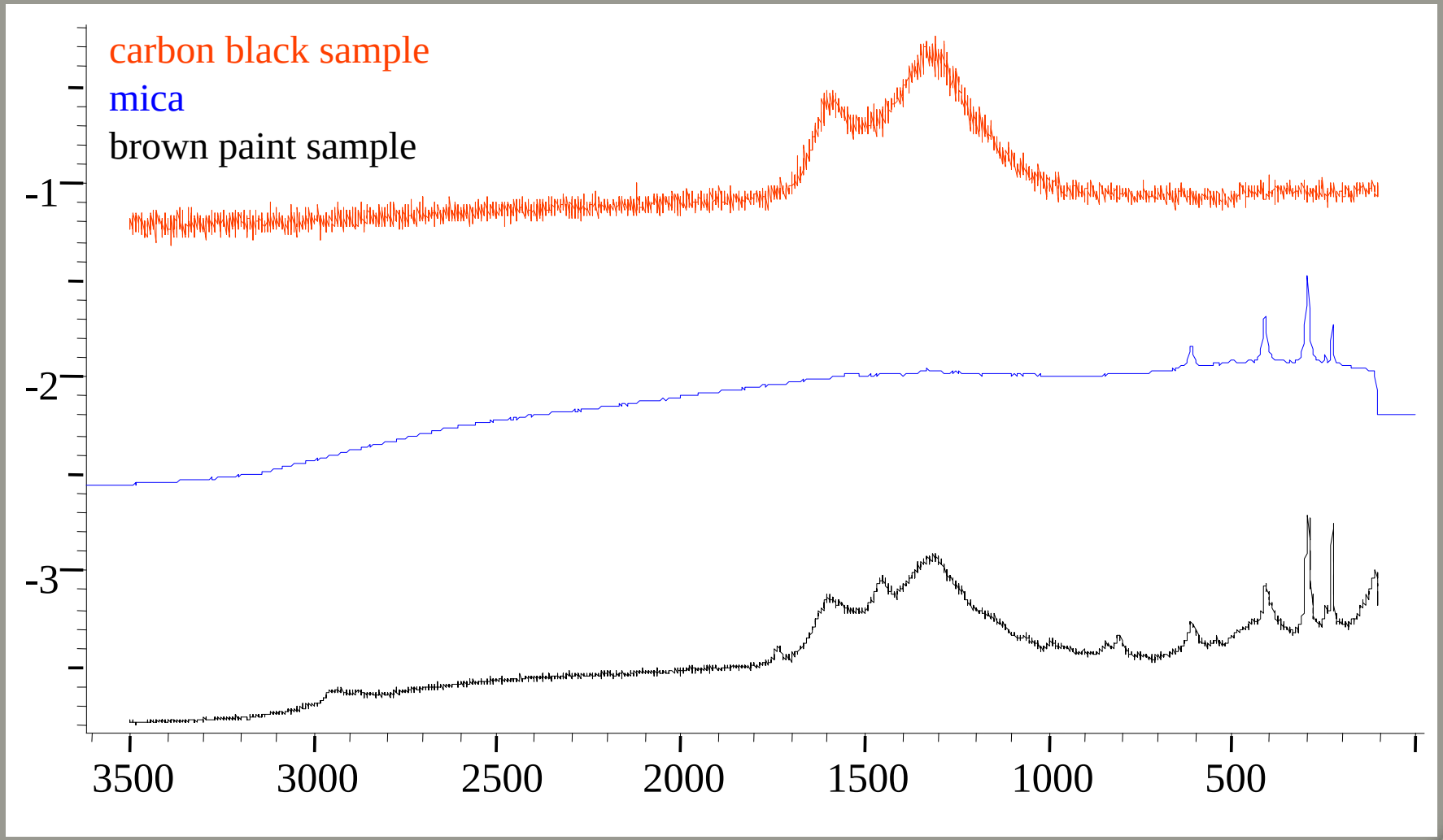
Black Paint:


carbon black sample
black paint sample
-2
-2.5
-3
-3.5
3500
3000
2500
2000
1500
1000
500

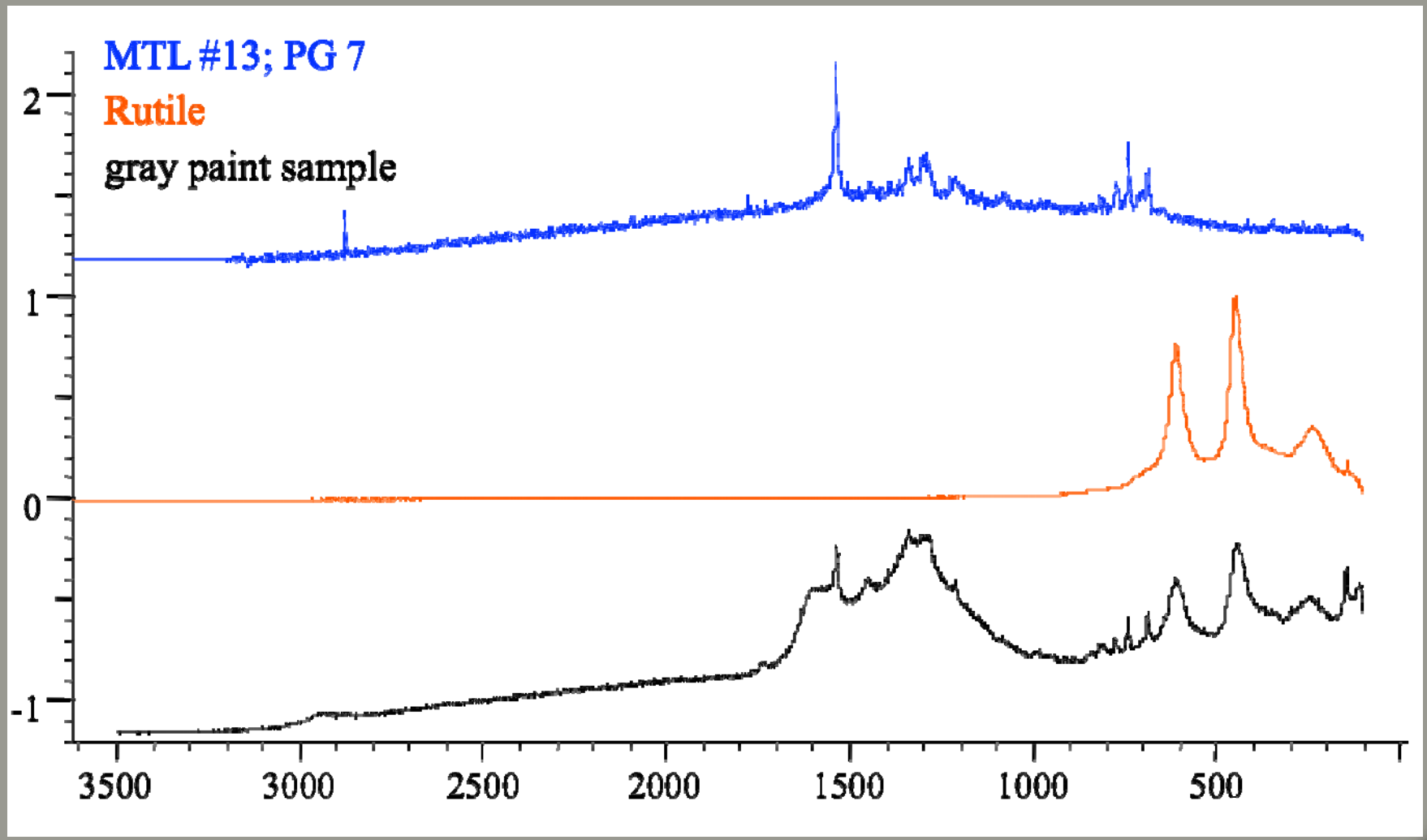
Green Paint:


PB 15:3
Yellow Iron Oxide
Green paint sample
0
-1
-2
3500
3000
2500
2000
1500
1000
500

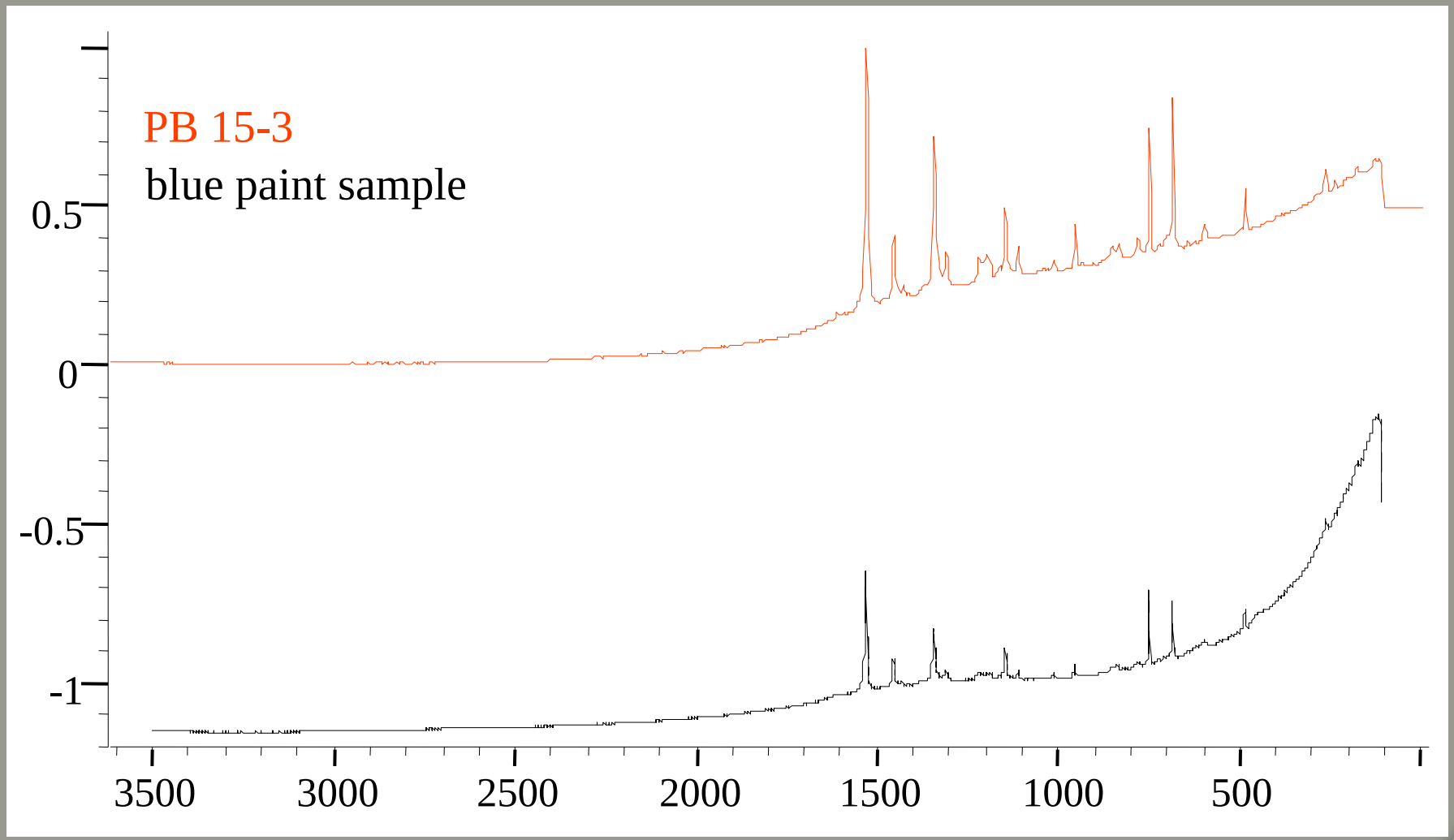
Brown Paint:


carbon black sample
mica
brown paint sample
-1
-2
-3
3500
3000
2500
2000
1500
1000
500

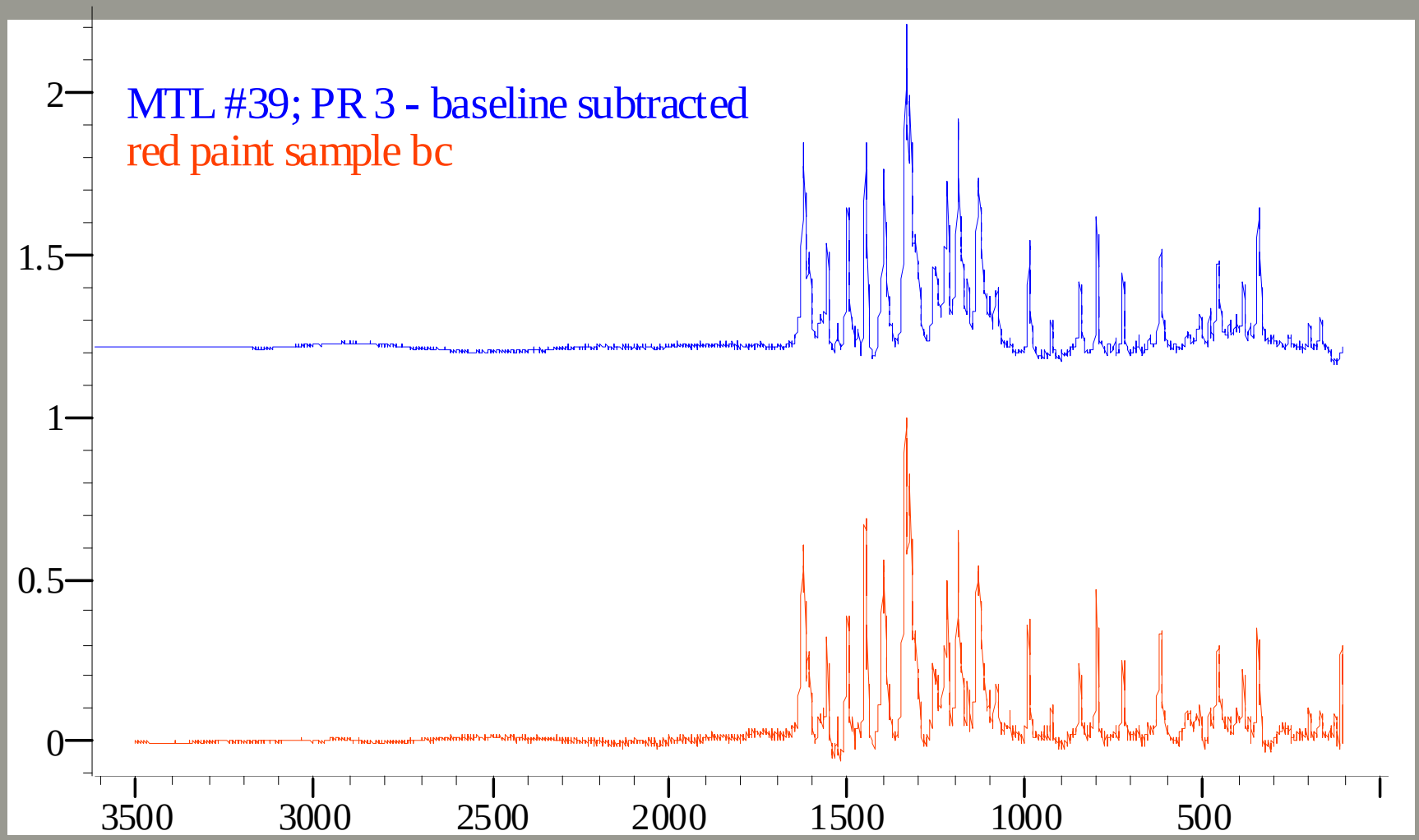
Gray Paint:


MTL #13; PG 7
Rutile
gray paint sample
2
1
0
-1
3500
3000
2500
2000
1500
1000
500

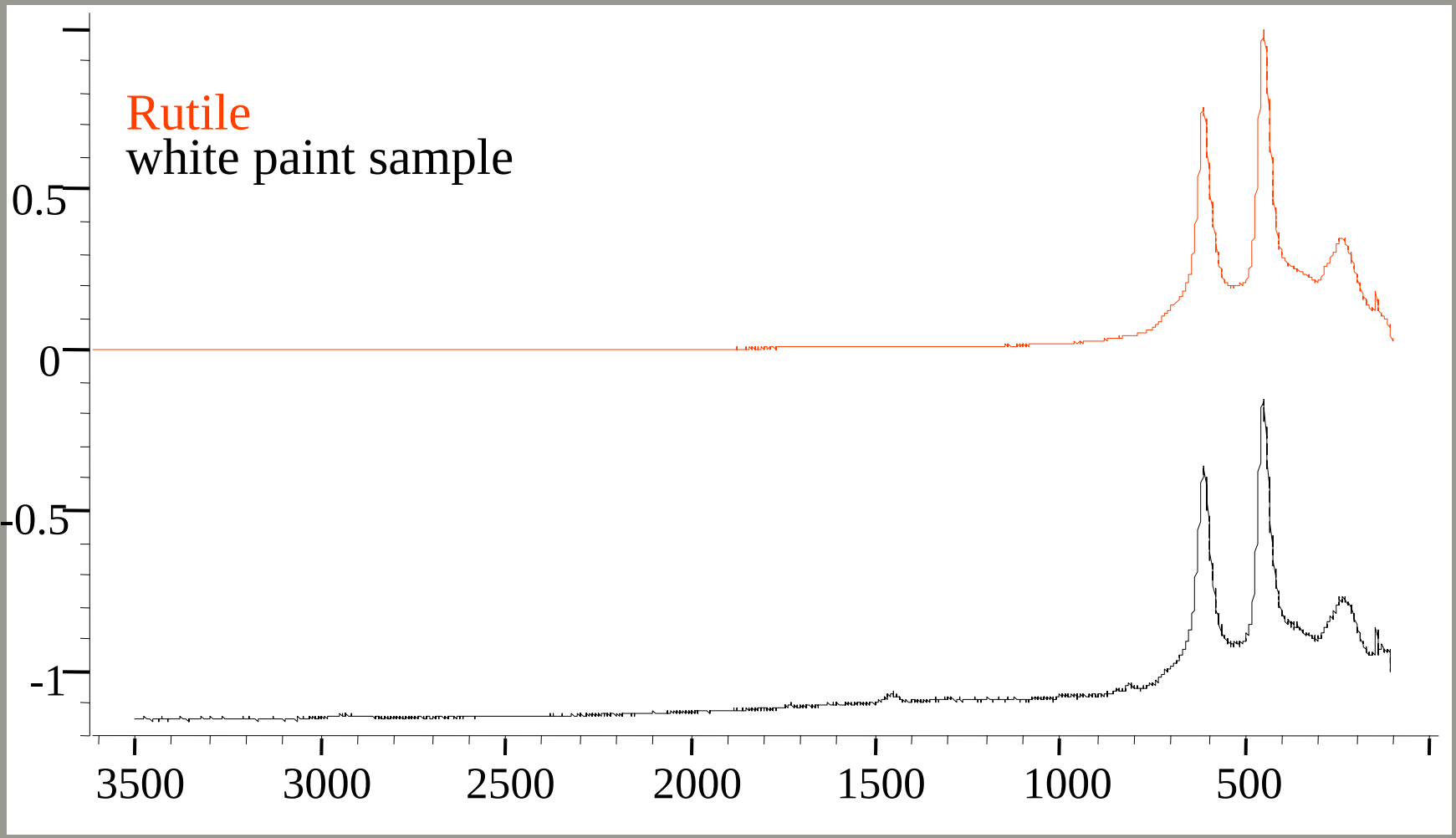
Blue Paint:


PB 15-3
blue paint sample
0.5
0
-0.5
-1
3500
3000
2500
2000
1500
1000
500

Red Paint:


MTL #39; PR 3 - baseline subtracted
red paint sample bc
2
1.5
1
0.5
0
3500
3000
2500
2000
1500
1000
500

White Paint:

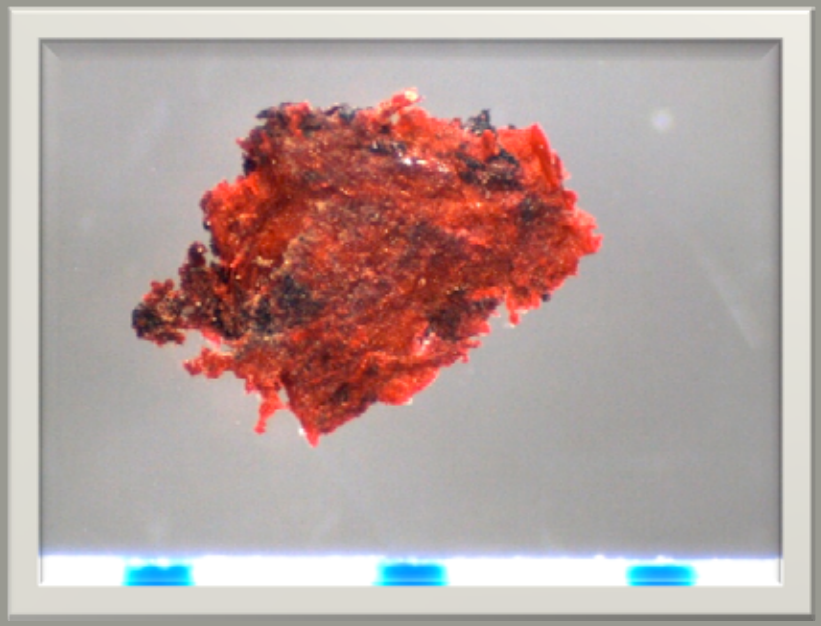

Rutile
white paint sample
0.5
0
-0.5
-1
3500
3000
2500
2000
1500
1000
500

Architectural Wrap –up:

- Seven paint samples studied
- Major pigments in all paints were identified
- Some fillers were identified
- Pigments not listed were identified
- In some cases, multiple pigments were identified
- Successful *in situ* identification

In Situ Analysis of Auto Paints

- No/limited sample preparation
- *In situ* analysis would allow reliable pigment ID
- What can we learn?
  - Major pigments
  - Minor pigments



Red paint flake
(scalebar in mm)

In Situ Analysis of Auto Paints

- 27 CTS Paint Samples
- Provided by Scott Ryland
- Emphasis on Browns and Reds (harder to examine)
- Some pigment names were supplied (from CTS)
- Analyzed and compared to our Raman Database

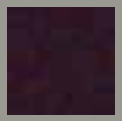
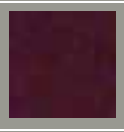
Blue Paint

- Blue 
  - 1 sample
  - Copper Phthalocyanine identified as being present by CTS
  - Raman identified Rutile, and PB 15:2 (Copper Phthalocyanine)

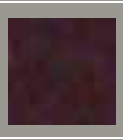
Yellow Paints

		Known Components (CTS supplied)	Components Identified by Raman
1.		• Benzimidazolone Yellow 4G	• Rutile • Do not have Yellow 4G reference
2.		• Benzimidazolone Yellow 3G	• Rutile • Benzimidazolone Yellow 3G
3.		• Isoindolinone Yellow 3R • Isoindolinone Yellow 3R	• Isoindolinone Yellow 3R • Rutile • Isoindolinone Yellow 3R
4.		• Benzimidazolone Yellow 3G	• Rutile • Rutile
5.		• Benzimidazolone Yellow 3G • Rutile • Hydrous Ferric Oxide	• Benzimidazolone Yellow 3G* *(similar to 3R with some distinct peak differences) • Rutile • Benzimidazolone Yellow 3G
6.		• Isoindolinone Yellow 3R	• Isoindolinone Yellow 3R • Rutile • **PG 36**
7.			

Red Paints (1 of 3)

		Known Components	Components Identified by Raman
1.		• Benzimidazolone Orange • Ferric Oxide • Rutile	• Benzimidazolone Orange • Rutile
2.		• Thioindigo Bordeaux • Hyd. Ferric Oxide	• Ferric Oxide • Carbon black • Rutile
3.		• ~~Quinacadine Red Y6~~ • Ferric Oxide • Perinone Orange • Thioindigo Bordeaux	• ~~Rutile~~ • Do not have Q-Red Y6 reference • Red Iron Oxide • ~~PR 88 ?~~
4.		• Benzimidazolone Brown	• Carbon black (no Benzimidizole Brown in ref. lib.)
5.		• DPP Red BO • Quinacridone Magenta B	• DPP Red BO • Do not have Q-Magenta B reference
6.		• Quinacridone Red Y • Benzimidazolone Orange • Ferric Oxide • Rutile	• Rutile • Benzimidazolone orange • Quinacridone Red Y • Red Iron Oxide (minor)
7.			

Red Paints (2 of 3)

		Known Components	Components Identified by Raman
8.		• Benzimidazolone Orange • Ferric Oxide	• Carbon black • Benzimidazolone orange • Red Iron Oxide
9.		• Magenta B • Mob Orange • Quinacridone Red Y	• Molybdate Orange • None
10.		• Isoindolinone Yellow 3R • Hyd. Ferric Oxide • Rutile and Mob Orange • Quinacridone Red Y • Ferric Oxide	• Fluorescence was a problem • Carbon black • Quinacridone red Y
11.		• Benzimidazolone Orange • Quinacadine Red Y6	• Benzimidazalone Orange • Rutile
12.		• Hyd. Ferric Oxide • Isoindolinone Yellow 3R	• Quinacadine Red
13.		• Benzimidazolone Brown	• Carbon black • DPP Red BO
14.			

Red Paints (3 of 3)

		Known Components	Components Identified by Raman
15.		• DPP Red BO • Quinacridone Magenta B	• DPP Red BO
16.		• Benzimidazolone Orange • Qunacridone Red Y	• Benzimidazolone Orange • Benzimidazolone Orange
17.		• Benzimidazolone Orange • Ferric Oxide • Qunacridone Violet • ~~Silica encapsulated Mob~~ Orange	• Qunacridone Red Y • Red Iron Oxide • Qunacridone Violet • ~~Molybdate Orange~~
18.		• Quinacridone Violet • Mob Orange	• Molybdate orange
19.			

Auto Paint Summary:

Out of 26 yellow and red paints studied:

- 15 different pigments identified *in situ*
- based on a database (at the time) of ~100 pigments
  (now ~200 pigments)
- not all pigments in database are automotive pigments
- Several pigments could not identified in these paints (not in our database)
- *As many as 4 pigments were identified IN SITU in a single sample*

Summary:

- Raman has the potential to be extremely valuable for identifying pigments *in situ*.
- Valuable for many other types of materials
- Since, we've expanded our database to >200 pigments
- Currently working on a general classification scheme
- Focus now on minor pigments

Thank You

- Microtrace Staff
- Heidi Bonta
- Scott Ryland

Questions???