CHARACTERIZATION AND DISCRIMINATION OF INKJET PRINTER INKS USING MICRO RAMAN SPECTROSCOPY

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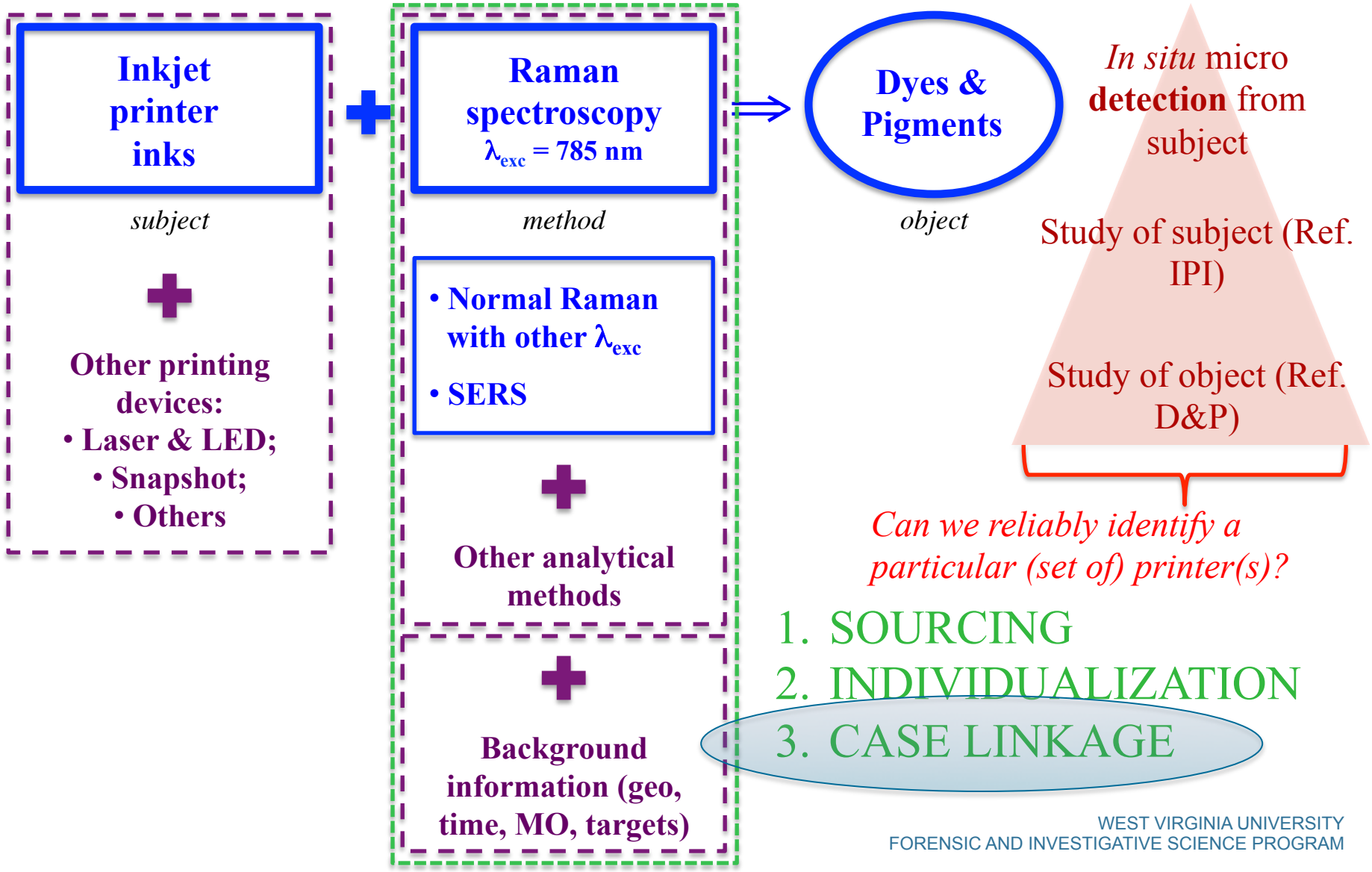
WEST VIRGINIA UNIVERSITY
FORENSIC AND INVESTIGATIVE SCIENCE PROGRAM

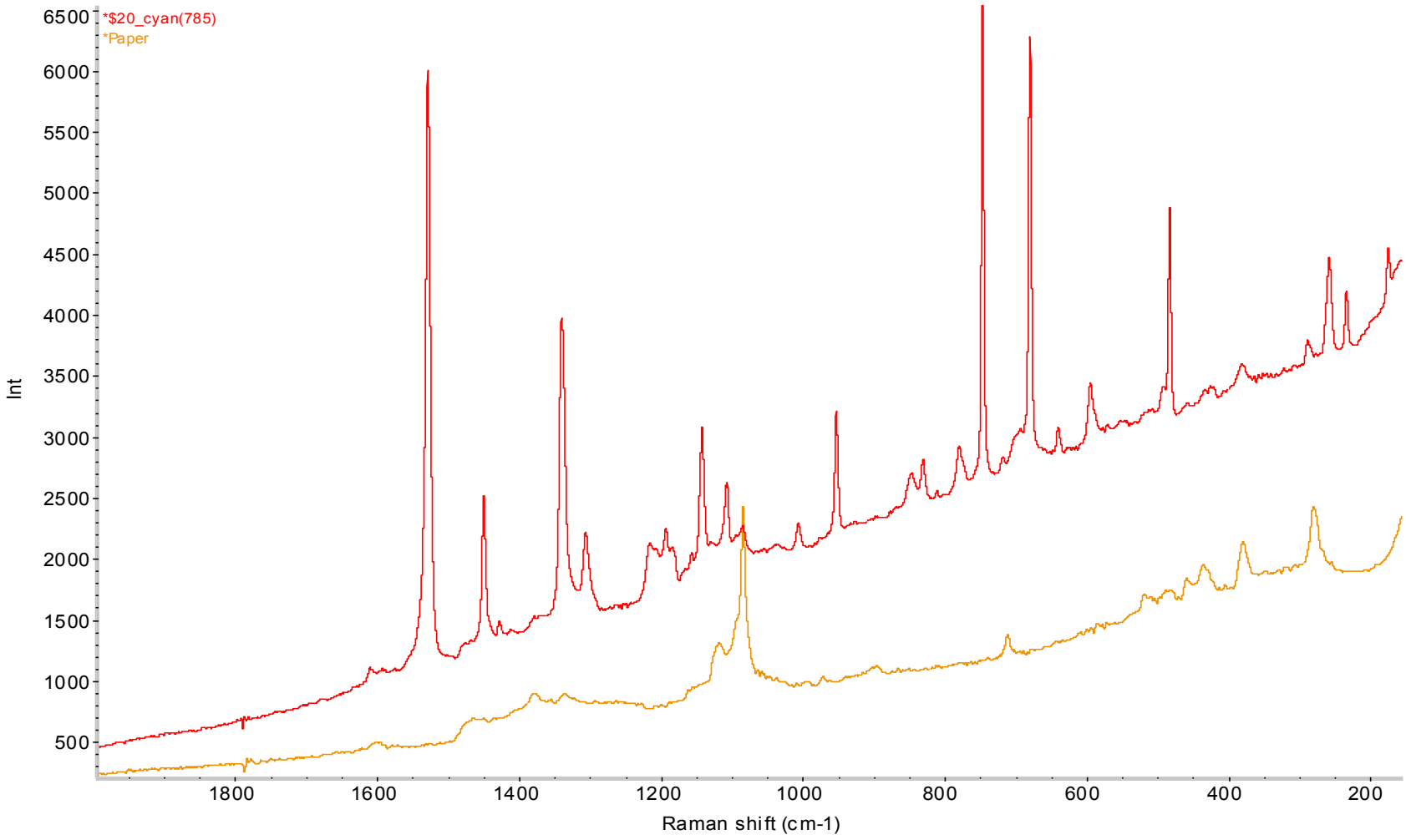
RESEARCH MAP



COUNTERFEITED $20 BANKNOTE

Provided by the Criminal Investigative Division, Treasury Obligations Section of the United States Secret Service (USSS)

CYAN SPOTS


*$20_cyan(785)
*Paper
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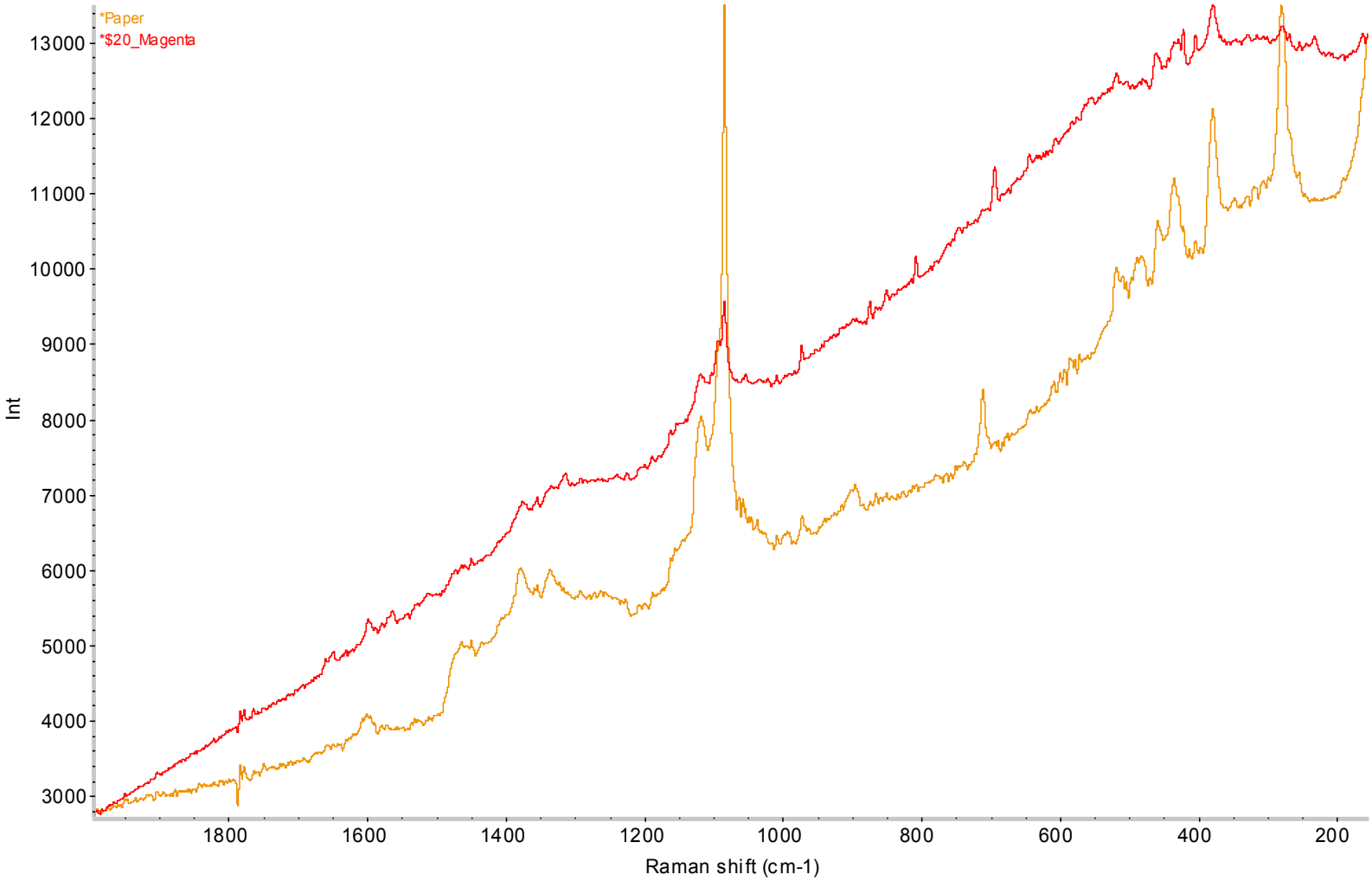
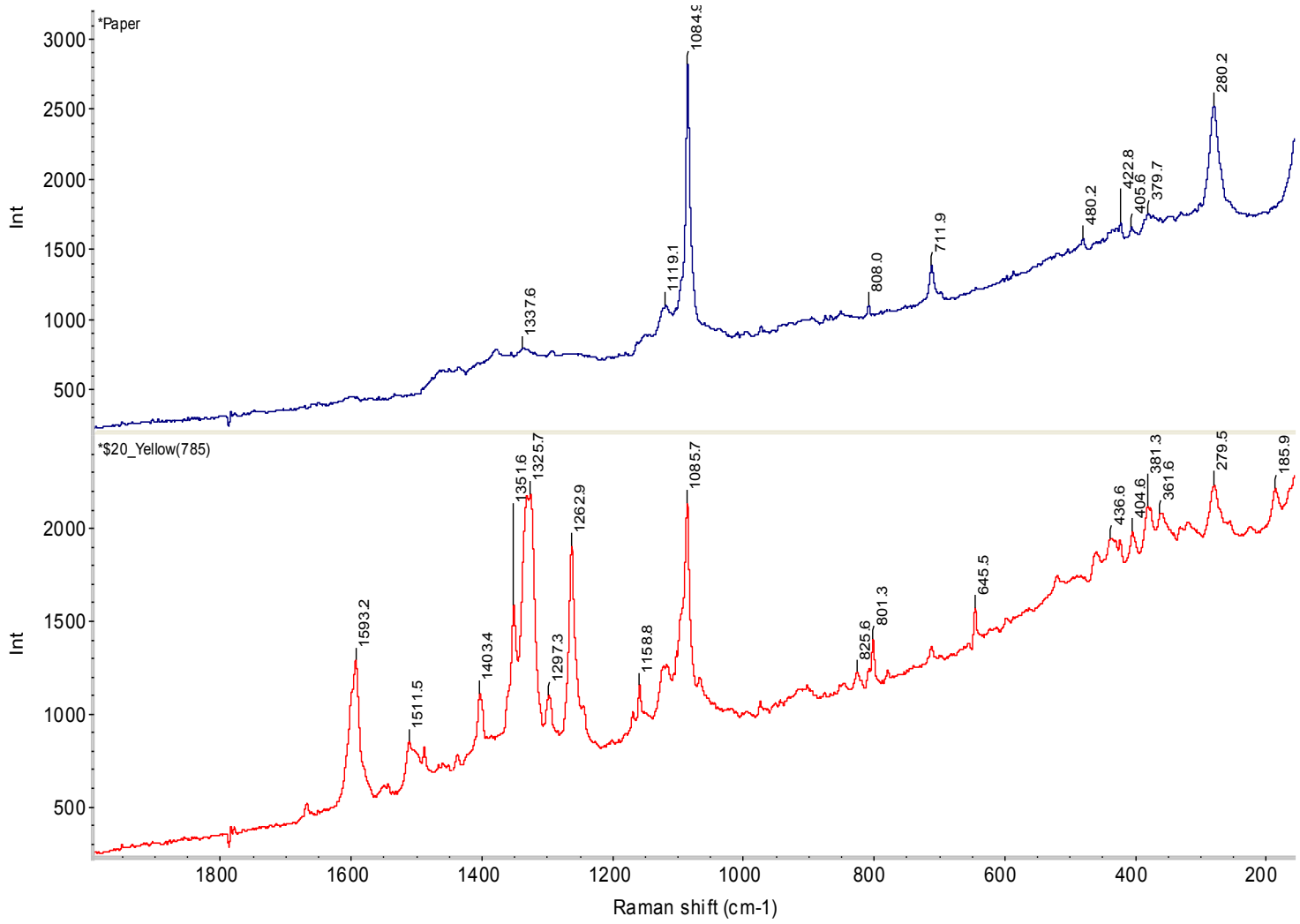
Raman shift (cm-1)

MAGENTA SPOTS



YELLOW SPOTS



WHY RAMAN SPECTROSCOPY?

- ~ Rapid;
- ~ Simple;
- *In situ* analysis;
- High resolution focalization (1 μm)
- Non destructive;
- Data suitable for database search

- Distinguish between dyes and pigments
- Excellent for pigment based inks

- Fluorescence
- Occasional paper interference
- Mostly, detects main colorant
  - Insensitive to mixtures

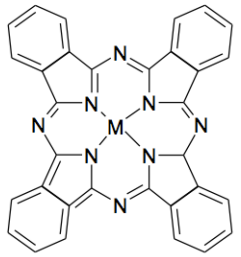
SAMPLES

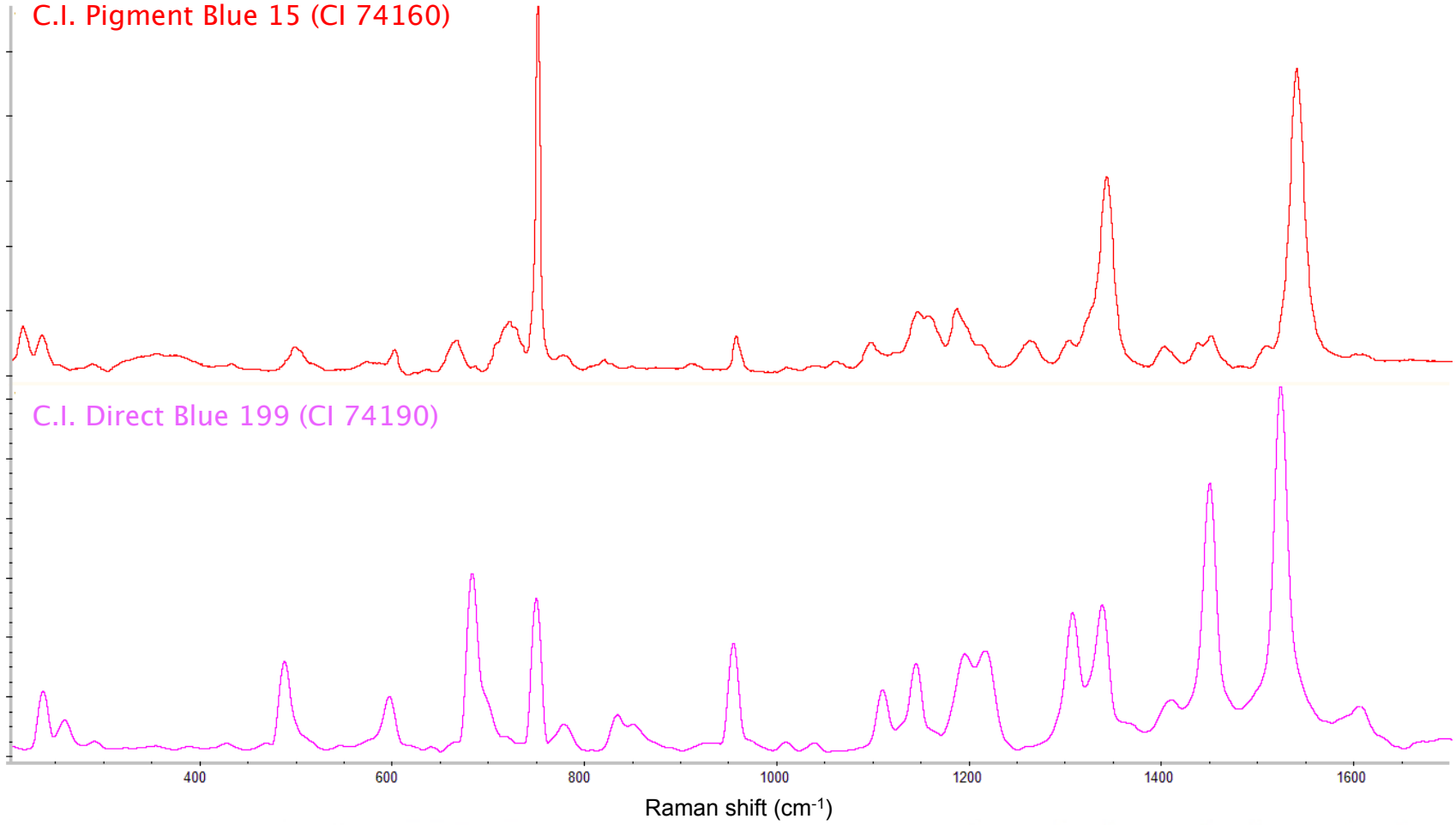
Manufacturer	Model	Cartridge or serial #	Extraction MeOH
HP	Officejet 6500	n/a	Dye
Epson	n/a	T0691	Pigment
Lexmark	228 2010 CE 81	100	Dye
Canon	PG 210XL	n/a	Dye
Canon	K10349	JWEA49509	Dye
HP	Officejet 6500	TH0AM210CV	Dye
HP	Deskjet F4180	CN7804520X	Dye
Brother	MFC-665CW	U61581A7F308871	Dye
Sensient	n/a	B18038	Dye

Samples provided by the Criminal Investigative Division, Treasury Obligations Section of the United States Secret Service (USSS).

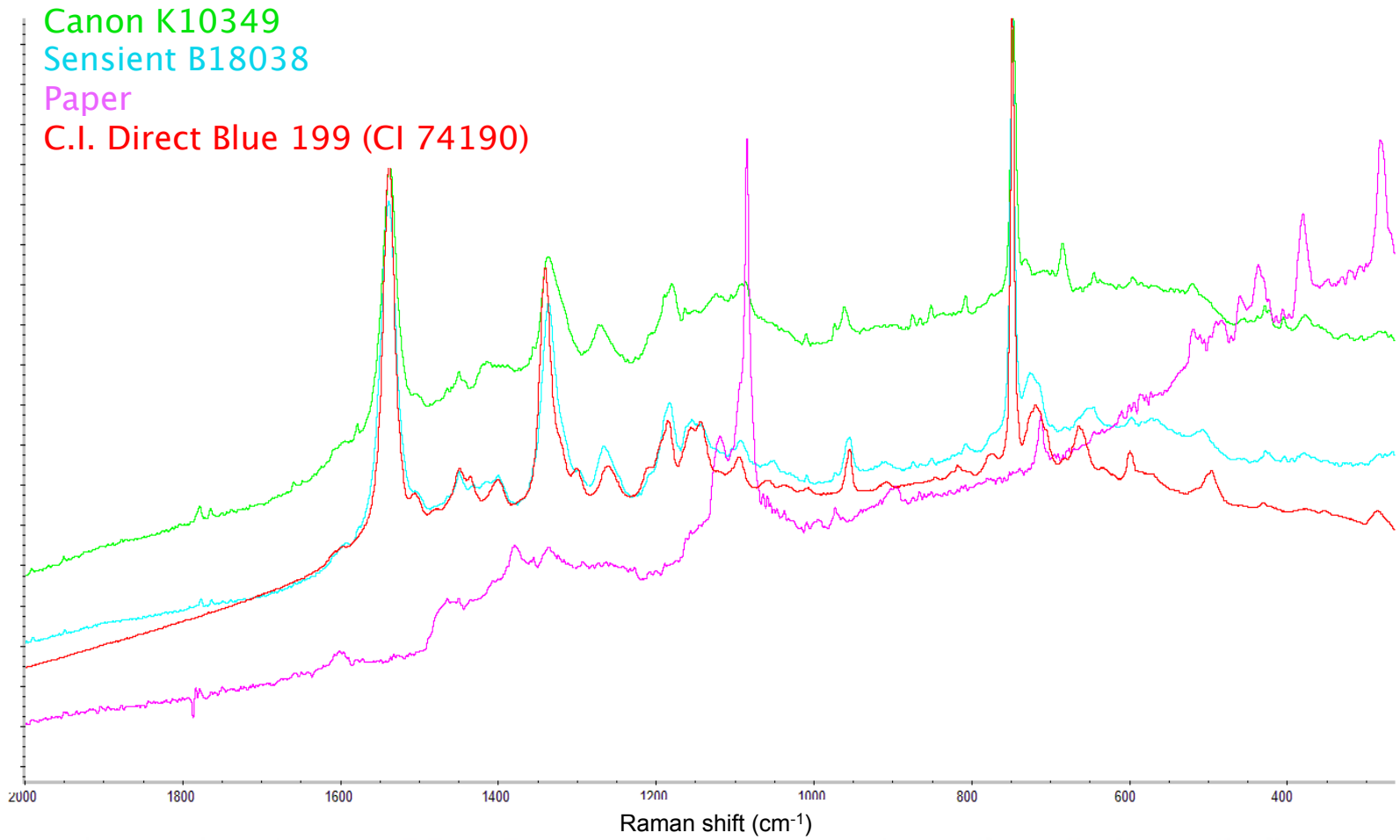
IDENTIFICATION OF COLORANTS

COLORANTS ID IN CYAN SPOTS





COLORANTS ID IN CYAN SPOTS



OPEN SOURCES

CI Name	CI Number	Concentration	Qua
Reactive Red 180	181055	100.00%	Salt-
Acid Blue 9	42090	165.00%	Low
Direct Blue199	74190	175.00%	Salt-
Acid Yellow 23	19140	200.00%	Salt-
Direct Black 168	30410	165.00%	Salt-
Direct Black 19	35255	200.00%	Salt-

Product Range

Product Name	C.I. No.
Acid RED-1	18050

SensiJet® Product	Chemical Class	Pigment Content	Lightfastness (1-8 Scale)
Magenta PV19	Azo	18%	4
Select Magenta PV19	Azo	10%	4
Select Magenta PR122	Azo/Triazine	10%	4
Yellow PY74	Azo	10%	5
Yellow PY155	Triphenylmethane	10%	2
Cyan PB15:3	Phthalocyanine	12%	5
Select Cyan PB 15:3	Xanthene	8%	2
Select Cyan PB 15:4	Azo	10%	3
Black PB94	Xanthene	10%	

Source: Sensient Technologies

Given here is a few of the inkjet dyes that are available in the powder form along with its characteristics:

Product	Chemical Class	Dye Content	Lightfastness (1-5 Scale)	Color
Acid Yellow 17	Azo	18%	4	
Acid Yellow 23	Azo	10%	4	
Direct Yellow 86	Azo/Triazine	10%	4	
Direct Yellow 132	Azo	10%	5	
Acid Blue 9	Triphenylmethane	10%	2	
Direct Blue 199	Phthalocyanine	12%	5	
Acid Red 52	Xanthene	8%	2	
Acid Red 249	Azo	10%	3	
Acid Red 289	Xanthene	10%	3	
Direct Red 227	Disazo	10%	2	
Reactive Red 31	Azo/Triazine	10%	3	
Reactive Red 120	Azo/Triazine	10%	2	
Reactive Red 180	Azo/Vinylsulfone	10%	3	
Direct Black 19	Azo	17%	4	
Reactive Black 8	Azo, Cr complex	14%	4	
Reactive Black 31	Azo/Vinylsulfone	10%	4	
Food Black 2	Azo	14%	3	

Source: Sensient Technologies

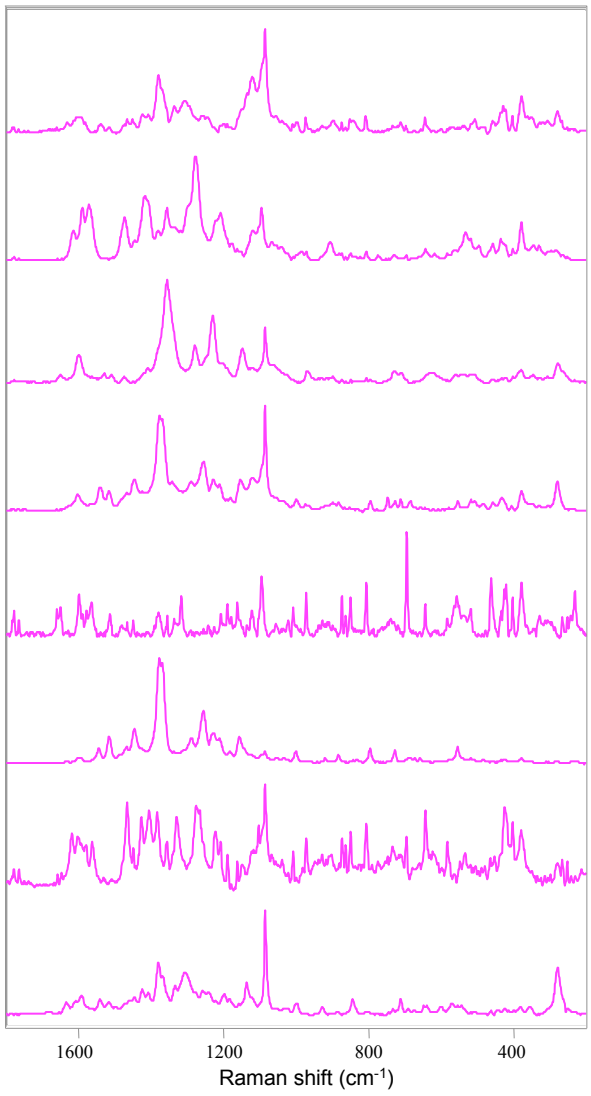
POLYMORPHISMS AND DIFFERENTIATIONS

VISUAL INSPECTION

Magenta
- Brother MFC-665CW (373) - HP Officejet 6500 (374)
- Canon K10349 (37)
- Sensient B20557 (301)
- HP Deskjet F4180 (372)
- Epson T0693 (381)
- HP Officejet 6500 (413)
- Lexmark 228 2010 CE 81 (441)
- Canon PG 210XL (452)

Yellow
- Canon K10349 (37) - Canon PG 210XL (452)
- HP Officejet 6500 (414) - HP Officejet 6500 (374)
- Sensient B17066 (311)
- HP Deskjet F4180 (372)
- Epson T0694 (382)
- Brother MFC-665CW (373)
- Lexmark 228 2010 CE 81 (442)

Cyan
- Lexmark 228 2010 CE (440) - Sensient B18038 (298) - HP Deskjet F4180 (372)
- HP Officejet 6500 (374) - HP Officejet 6500 (412) - Brother MFC-665CW (373)
- Epson T0692 (380)
- Canon K10349 (37)
- Canon PG 210XL (452)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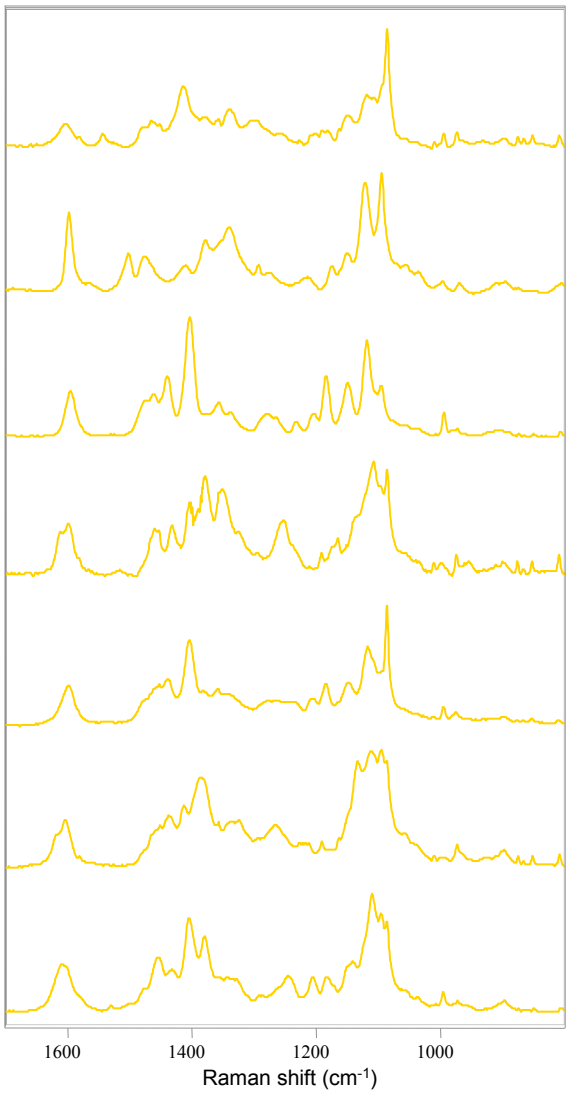
Raman shift (cm-1)


1600
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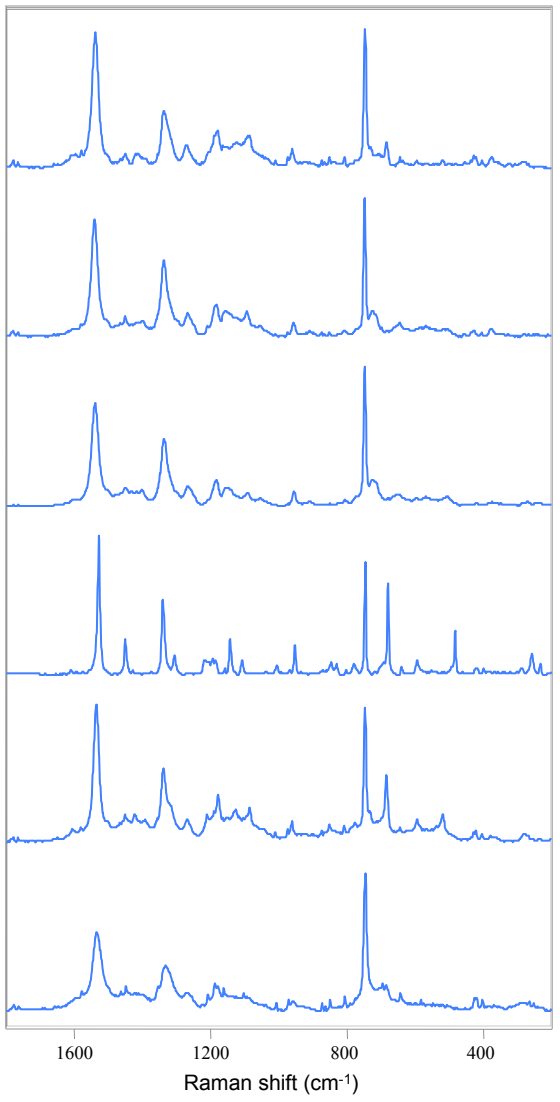
1000
Raman shift (cm-1)


1600
1200
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400
Raman shift (cm-1)

PREVIOUS STUDY

22 colored ink-jet printers inks available on the Swiss market (NIR 785 nm)

- Magenta: 11 groups
- Yellow: weak scattering + paper interference
- Cyan: not discriminatory

Mazzella W, Mathieu A, Buzzini P. Micro-Raman Spectroscopy of Color Inkjet Printed Documents. *Journal of the American Society of Questioned Document Examiners* (ASQDE) 2006; 9(1): 1-8

DATA ANALYSIS

Pre-treatment

a) Normalization
b) Baseline correction
c) Standardization
d) 1st derivative + smoothing (Savitzky-Golay)
e) Multiplicative Scatter Correction (MSC)
f) Standard Normal Variate (SNV)

Variable selection

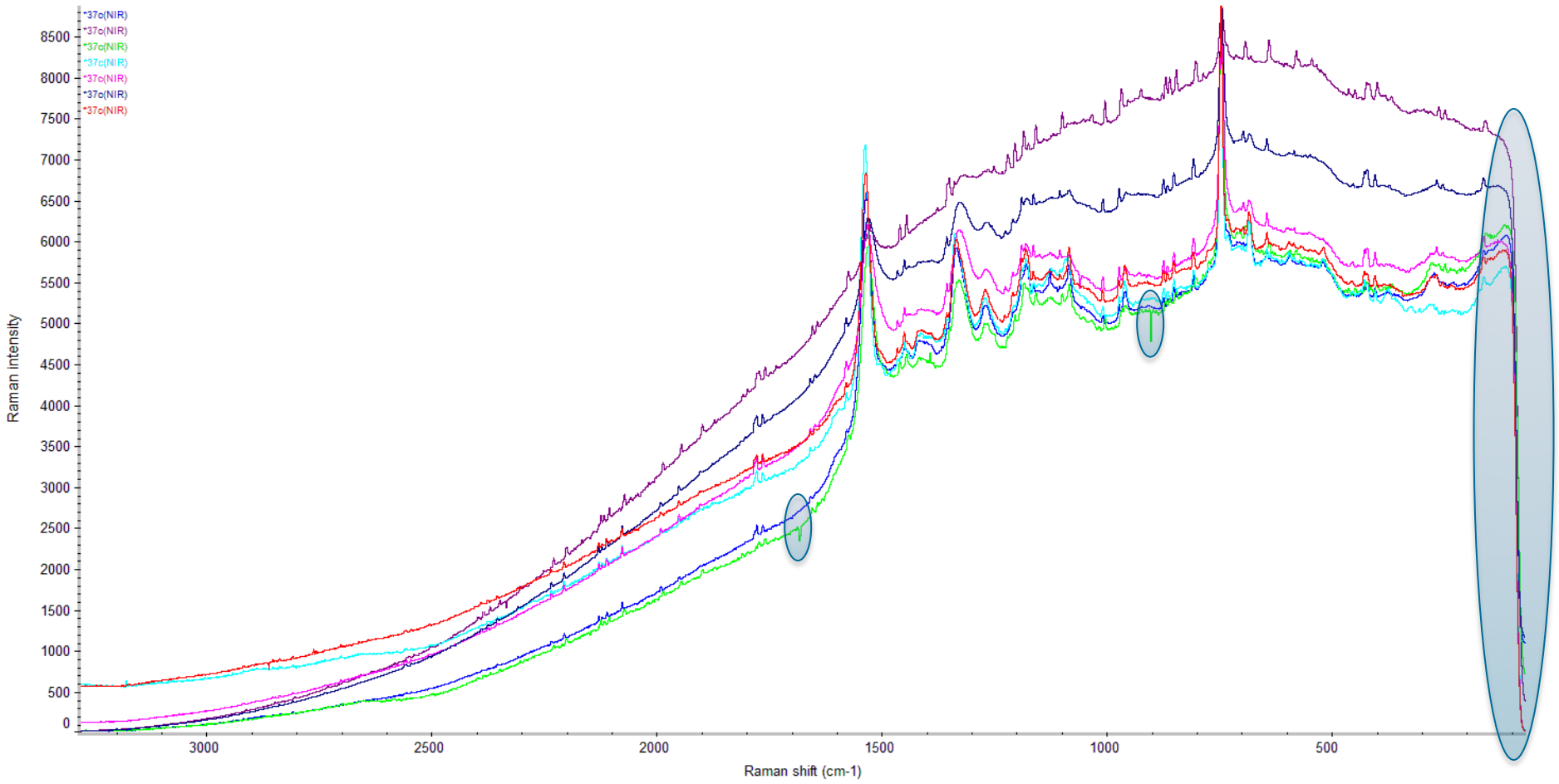
Exploratory techniques

a) PCA
b) Cluster analysis
- Distance (Euclidean, Manhattan)
- Correlation (Pearson, cosine)
  a) Hierarchical (dendograms)
  b) Partitioning

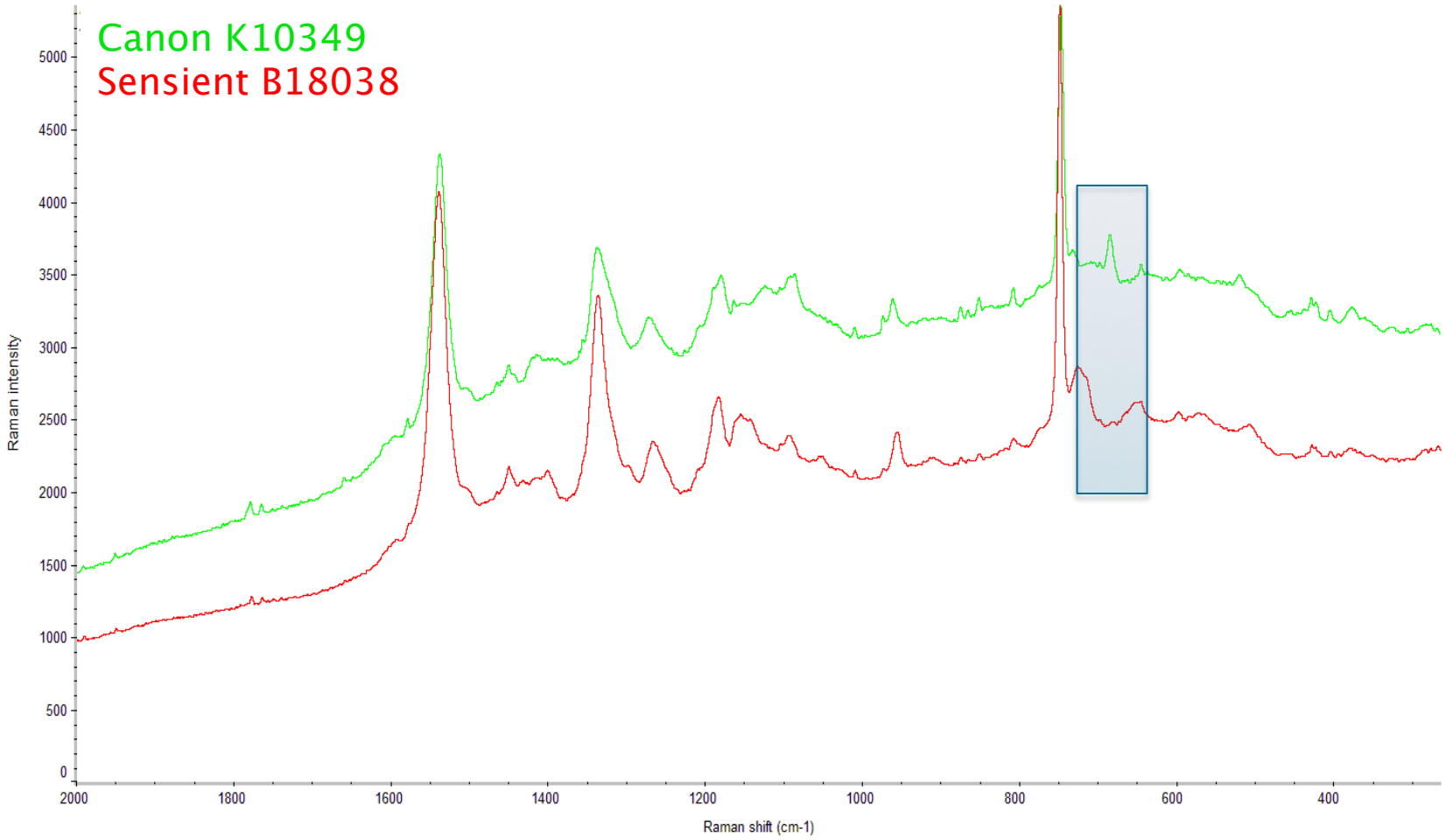
Discriminant analysis

a) Linear discriminant analysis
b) Quadratic discriminant analysis
c) K Nearest Neighbor (KNN)
d) Partial Least Squares (PLS)
e) Soft Indep. Modeling of Class Analogy (SIMCA)
f) Support Vector Machines (SVM)

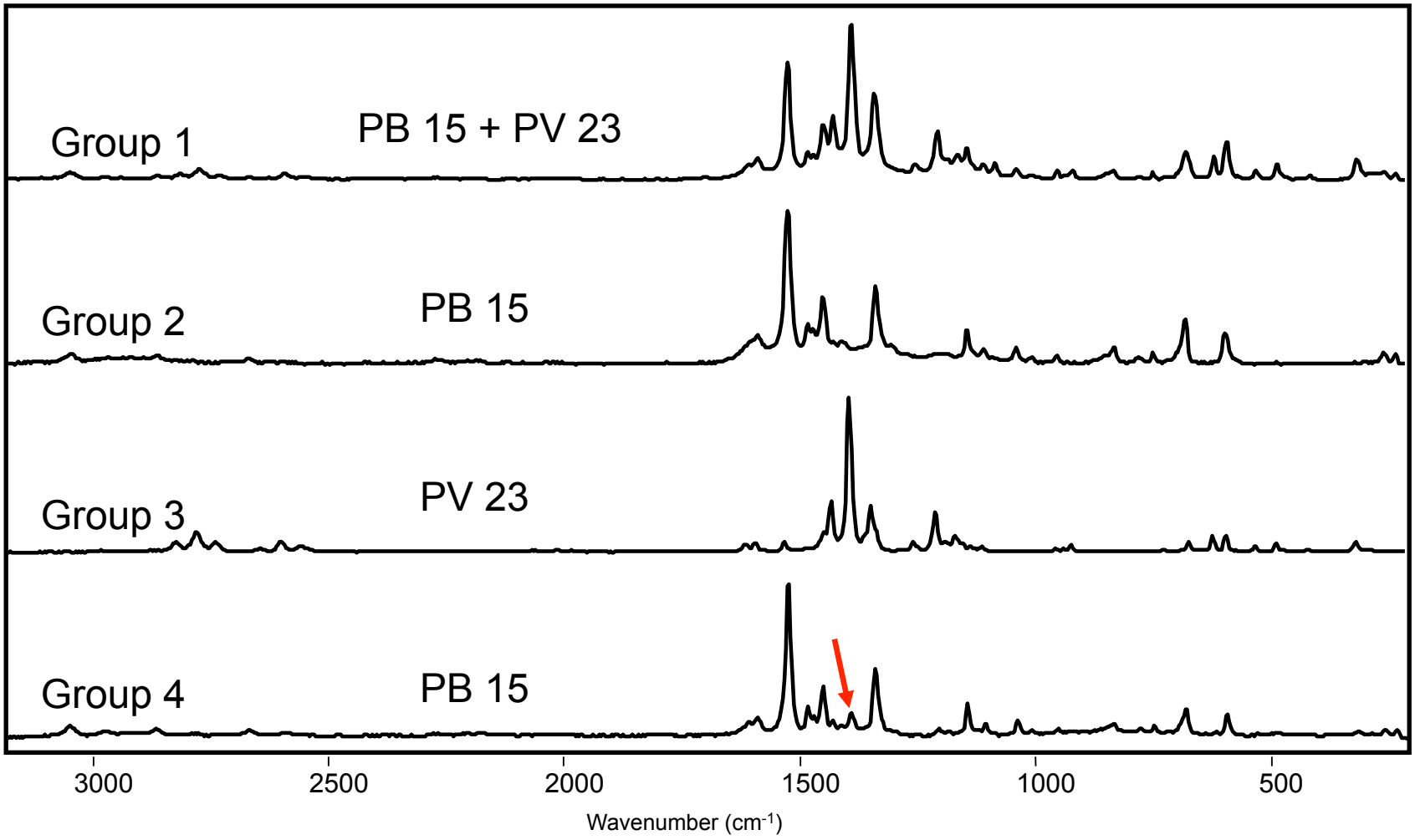
CYAN SPOTS – CANON K10349



CYAN SPOTS - DIFFERENTIATIONS

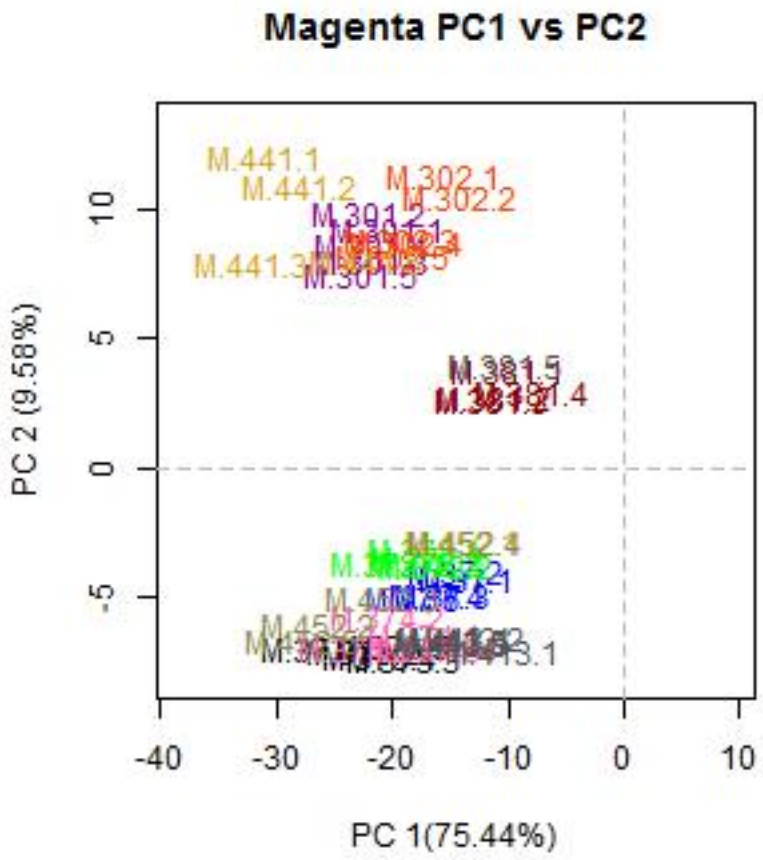


Argon ion laser (514.5 nm): 4 groups

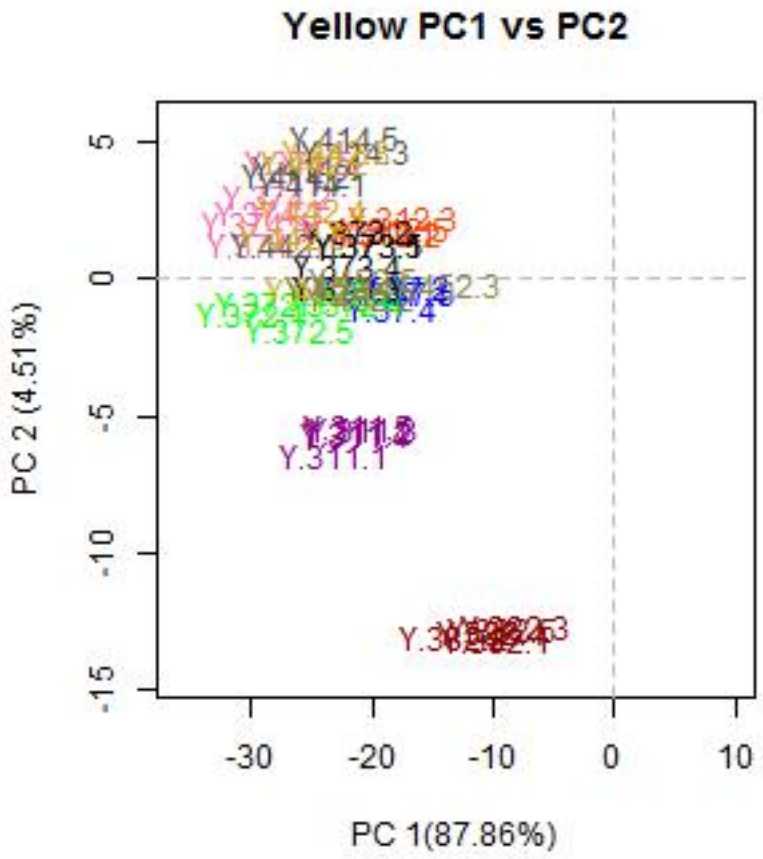


Source: Mazzella W, Buzzini P. Raman Spectroscopy of Blue Gel Pen Inks. *Forensic Science International* 2005; 152; 2-3: 241-247.

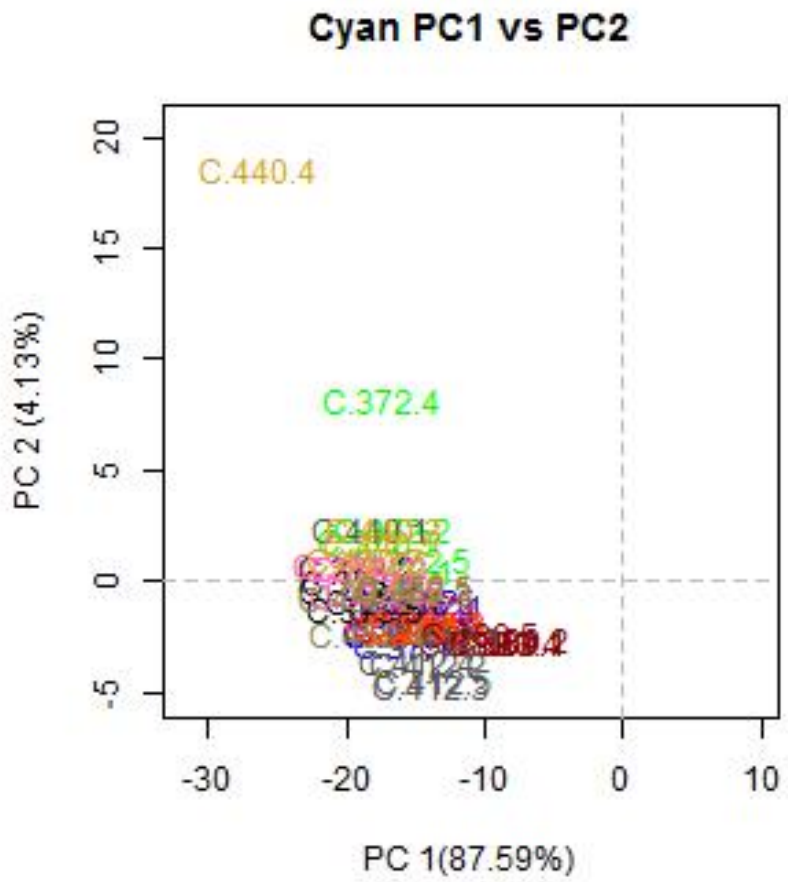
PCA – MAGENTA SPOTS



PCA – YELLOW SPOTS



PCA - CYAN SPOTS



THE $20 COUNTERFEIT EXAMPLE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THE UNITED STATES OF AMERICA
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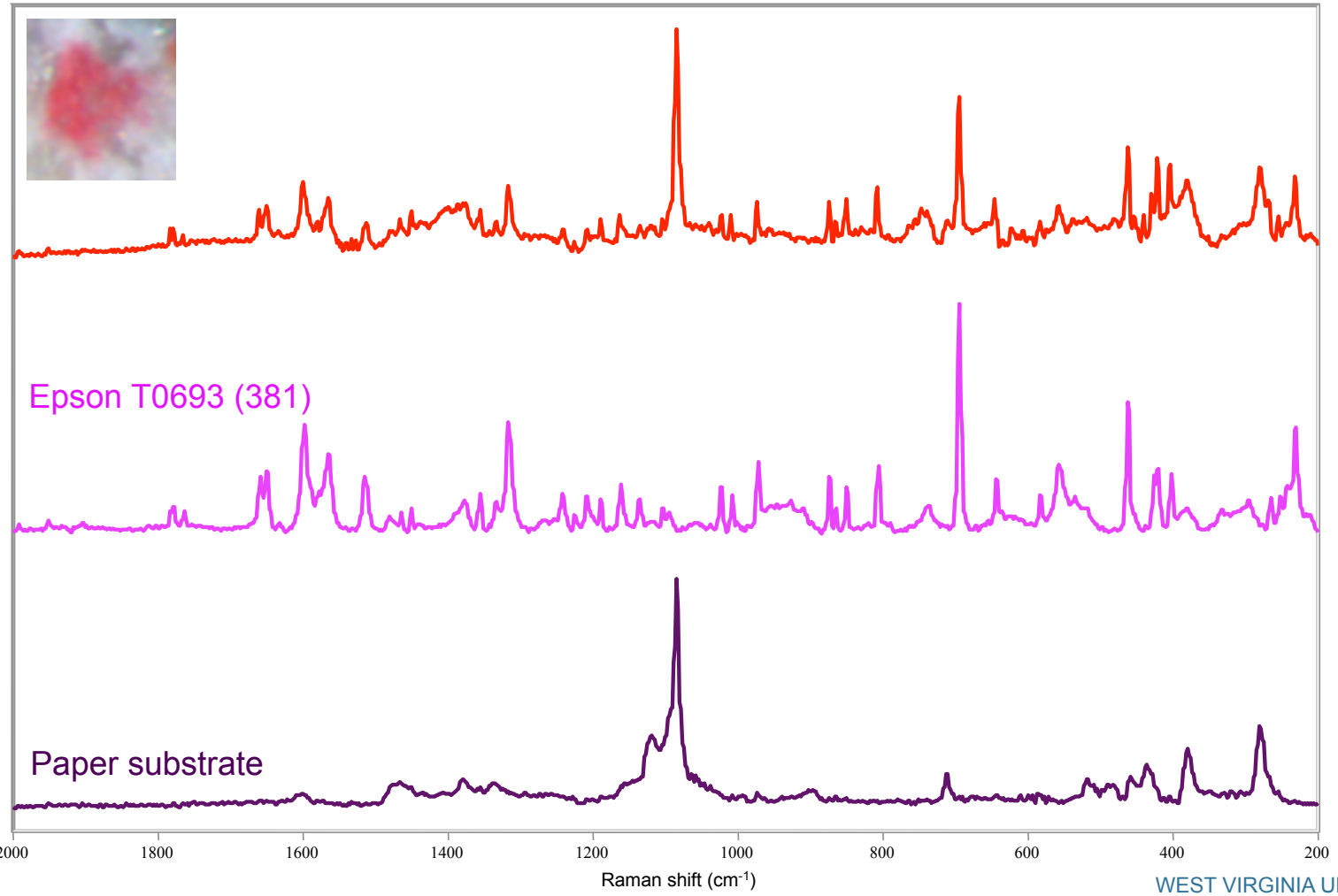
SERIES 2004 A
TWENTY DOLLARS


Epson T0693 (381)
Paper substrate
2000
1800
1600
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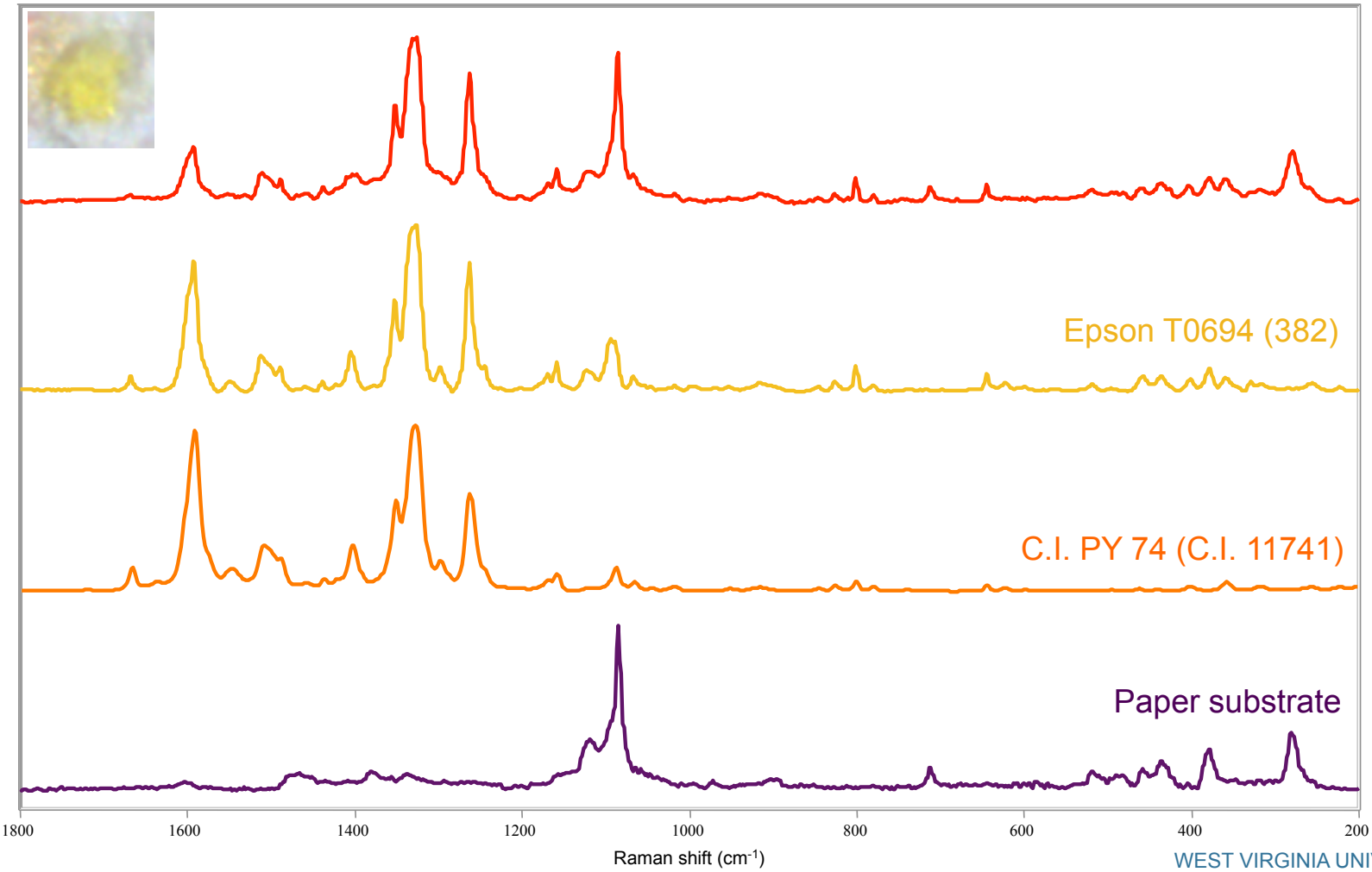
200
Raman shift (cm-1)


20
FEDERAL RESERVE NOTE
GA 75625785 A
A1
THE UNITED STATES OF AMERICA
GA 75625785 A
SERIES 2004 A
TWENTY DOLLARS
JACKSON


Epson T0694 (382)
C.I. PY 74 (C.I. 11741)
Paper substrate
1800
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Raman shift (cm-1)


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A1
THE UNITED STATES OF AMERICA
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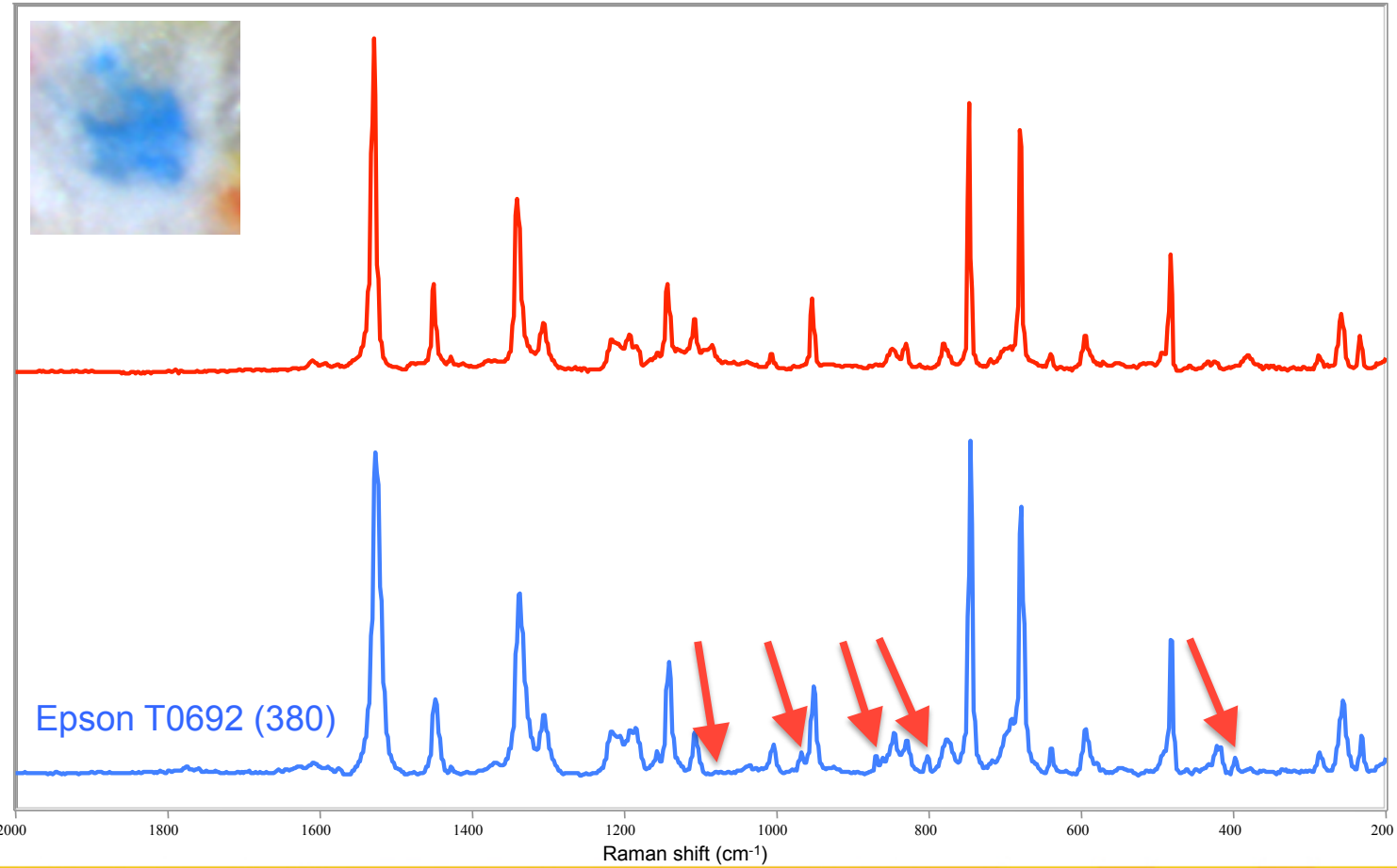
Epson T0692 (380)
2000
1800
1600
1400
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Raman shift (cm-1)

FUTURE WORK

- Increase dataset (CYM);
- Black inks;
- Non OEM;
- Other laser wavelengths;
- Analyze extracts and paper support after extracts;
- Development of tailored chemometric approach.

ACKNOWLEDGMENTS

- Kerre Corbin, USSS
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- Kelley Harris, former USSS