CHARACTERIZATION AND DISCRIMINATION OF INKJET PRINTER INKS USING MICRO RAMAN SPECTROSCOPY

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67th Annual Scientific Meeting of the American Academy of Forensic Sciences
Orlando, FL
February 16-21, 2015
RESEARCH MAP

Inkjet printer inks

Raman spectroscopy $\lambda_{\text{exc}} = 785 \text{ nm}$

Dyes & Pigments

In situ micro detection from subject

Study of subject (Ref. IPI)

Other printing devices:
- Laser & LED;
- Snapshot;
- Others

Other analytical methods
- Normal Raman with other $\lambda_{\text{exc}}$
- SERS

Can we reliably identify a particular (set of) printer(s)?

1. SOURCING
2. INDIVIDUALIZATION
3. CASE LINKAGE

Background information (geo, time, MO, targets)

Study of object (Ref. D&P)
COUNTERFEITED $20 BANKNOTE

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

![Graph showing Raman shift vs. intensity for cyan spots and paper samples.](image-url)
MAGENTA SPOTS
YELLOW SPOTS

**Graph:**
- **Y-axis:** Int
- **X-axis:** Raman shift (cm⁻¹)
- Peaks at various wavenumbers indicated:
  - 1932, 1611.5, 1403.4, 1351.6, 1297.3, 1252.3, 1158.8, 1119.1, 1085.7, 1042.5, 864.5, 645.5, 486.6, 426.8, 391.3, 361.8, 301.3, 279.5, 185.9
  - Additional peaks marked as Paper and $20_Yellow(785)"
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

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Model</th>
<th>Cartridge or serial #</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP</td>
<td>Officejet 6500</td>
<td>n/a</td>
</tr>
<tr>
<td>Epson</td>
<td>n/a</td>
<td>T0691</td>
</tr>
<tr>
<td>Lexmark</td>
<td>228 2010 CE 81</td>
<td>100</td>
</tr>
<tr>
<td>Canon</td>
<td>PG 210XL</td>
<td>n/a</td>
</tr>
<tr>
<td>Canon</td>
<td>K10349</td>
<td>JWEA49509</td>
</tr>
<tr>
<td>HP</td>
<td>Officejet 6500</td>
<td>TH0AM210CV</td>
</tr>
<tr>
<td>HP</td>
<td>Deskjet F4180</td>
<td>CN7804520X</td>
</tr>
<tr>
<td>Brother</td>
<td>MFC-665CW</td>
<td>U61581A7F308871</td>
</tr>
<tr>
<td>Sensient</td>
<td>n/a</td>
<td>B18038</td>
</tr>
</tbody>
</table>

**Extraction**
- MeOH

**Dye**
- Pigment
- Dye
- Dye
- Dye
- Dye
- Dye
- 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

C.I. Pigment Blue 15 (CI 74160)

C.I. Direct Blue 199 (CI 74190)

Raman shift (cm$^{-1}$)
COLORANTS ID IN CYAN SPOTS

Canon K10349
Sensient B18038
Paper
C.I. Direct Blue 199 (CI 74190)
OPEN SOURCES

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

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

Source: Sensient Technologies
POLYMORPHISMS AND DIFFERENTIATIONS
### VISUAL INSPECTION

<table>
<thead>
<tr>
<th>Magenta</th>
<th>Yellow</th>
<th>Cyan</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Brother MFC-665CW (373)</td>
<td>- Canon K10349 (37)</td>
<td>- Lexmark 228 2010 CE (440)</td>
</tr>
<tr>
<td>- HP Officejet 6500 (374)</td>
<td>- Canon PG 210XL (452)</td>
<td>- Sensient B18038 (298)</td>
</tr>
<tr>
<td>- Canon K10349 (37)</td>
<td>- HP Officejet 6500 (414)</td>
<td>- HP Officejet 6500 (374)</td>
</tr>
<tr>
<td>- Sensient B20557 (301)</td>
<td>- HP Officejet 6500 (374)</td>
<td>- Sensient B17066 (311)</td>
</tr>
<tr>
<td>- HP Deskjet F4180 (372)</td>
<td>- HP Deskjet F4180 (372)</td>
<td>- HP Deskjet F4180 (372)</td>
</tr>
<tr>
<td>- Epson T0693 (381)</td>
<td>- Epson T0694 (382)</td>
<td>- Epson T0692 (380)</td>
</tr>
<tr>
<td>- HP Officejet 6500 (413)</td>
<td>- Brother MFC-665CW (373)</td>
<td>- Canon K10349 (37)</td>
</tr>
<tr>
<td>- Lexmark 228 2010 CE 81 (441)</td>
<td>- Lexmark 228 2010 CE 81 (442)</td>
<td>- Canon PG 210XL (452)</td>
</tr>
<tr>
<td>- Canon PG 210XL (452)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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

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
Argon ion laser (514.5 nm): 4 groups

Group 1: PB 15 + PV 23
Group 2: PB 15
Group 3: PV 23
Group 4: PB 15

Wavenumber (cm\(^{-1}\))

PCA – MAGENTA SPOTS
PCA – YELLOW SPOTS
PCA - CYAN SPOTS
THE $20 COUNTERFEIT EXAMPLE
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
• Sue Fortunato, USSS
• Yvette Monson, former USSS
• Kelley Harris, former USSS