

THE ROLE OF REFERENCE COLLECTIONS IN TRACE EVIDENCE

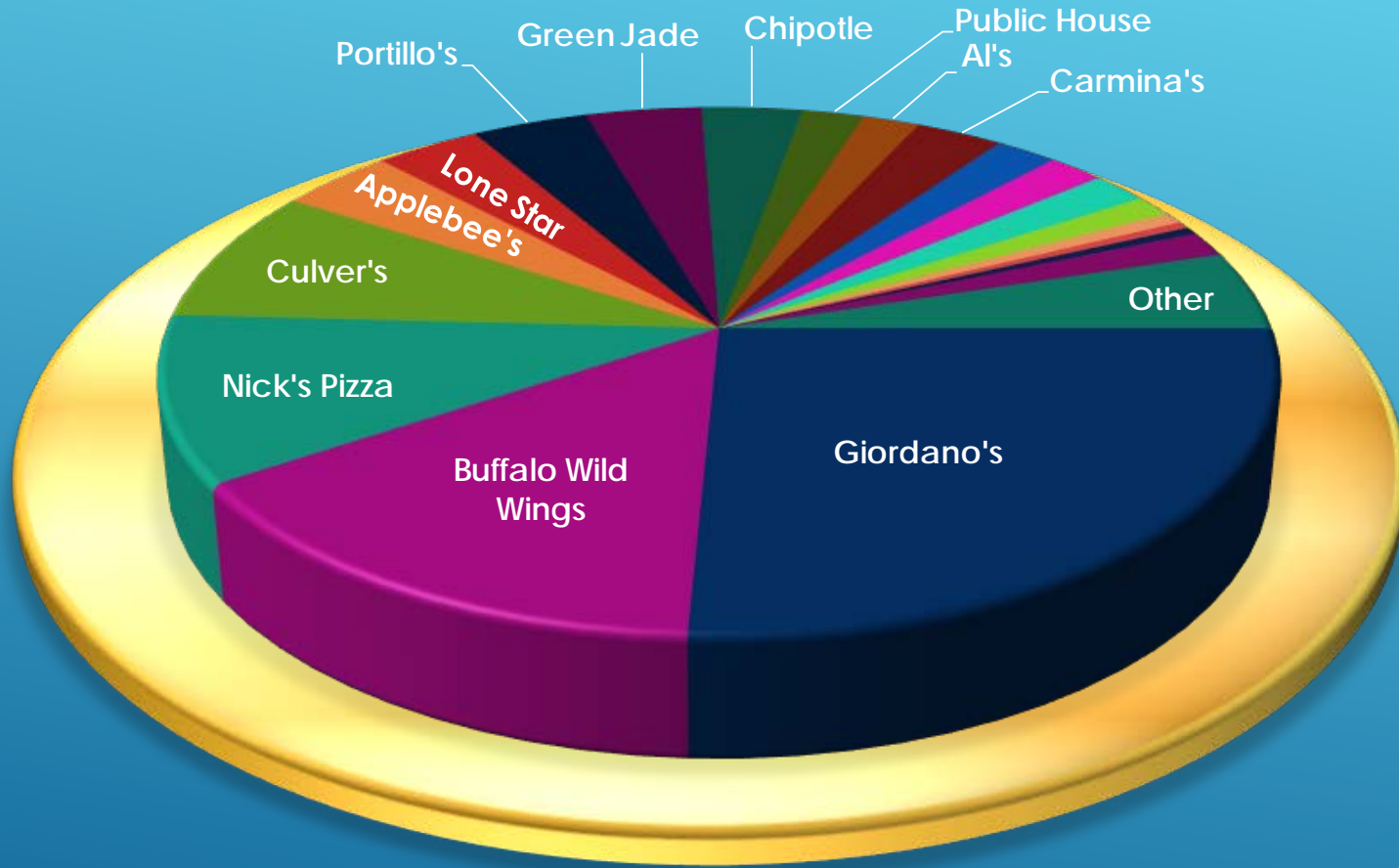
Christopher S Palenik, Ph.D.



www.microtracellc.com



MICROTRACE LUNCHESES (2011-2016)




n = 1149







List maintained by Jason Beckert



EARLY DATABASES



Microtrace— Fiber Reference Database

 New Record Sort   Back  Forward  Find Go to Labels 

ACETATE

Fiber ID #: AC-0031

Manufacturer Information

Trade Name:

Mfg Number:

Manufacturer:

Date Acquired:

Source:

Fiber Information

Color (nominal):

Color (mfr):

Color (old value):

Cross Section:

Denier:


Delusterant:

Collected Data

IR: X-Section: XS Image: Additional Data on File Yes No

Notes: Yarn. See AC file for extensive optical data.


Cross Section Image:



50 microns

Audit Log

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RELATIONAL DATABASES

Microtrace^{LLC} Colorant Database

Ascension Information		NIJ MT10-0135	<input type="checkbox"/> Yes			
Ascension Number	<input type="text" value="C-00012"/>	Number Only	<input type="text" value="00012"/>	FBI Set	<input type="checkbox"/> Yes	
Temp Ascension Number	<input type="text" value="00606"/>				Used in MT12-0118	<input type="checkbox"/> Yes
PD-Number	<input type="text" value="Pigment-PD-0249"/>				Used in MT12-0119	<input type="checkbox"/> Yes
Physical Sample	<input checked="" type="radio"/> Yes <input type="radio"/> No	Subsampled	<input type="radio"/> Yes <input type="radio"/> No			
Remainder Sample	<input type="radio"/> Yes <input checked="" type="radio"/> No	Slide Preparation	<input type="radio"/> Yes <input type="radio"/> No			
NDA Agreement	<input type="radio"/> Yes <input checked="" type="radio"/> No	NDA Expiration Date	<input type="text"/>			

Category Information	
Chemical Category	<input type="text" value="Colorant - Pigments - Inorganic - Silicate"/>
Category (New)	<input type="text" value="Colorant - Pigments - Inorganic - Oxide"/>

Colour Index Information	
C.I. Generic Name	<input type="text" value="C.I. Pigment White 27"/>
C.I. Class	<input type="text" value="Pigment"/> ▾
C.I. Color	<input type="text" value="White"/> ▾
C.I. Number	<input type="text" value="27"/>
C.I. Colon	<input type="text"/>
CrystalForm	<input type="text"/>
Colorant Strength	<input type="text"/>
Generic Name	<input type="text" value="Silica"/>
Constitution Number	<input type="text" value="77811"/>
Alt. Constitution Number	<input type="text"/>



RELATIONAL DATABASES

Microtrace_{LLC}
Colorant Database

Compositional Information

Structure



Chemical Name

Chemical Composition

Molecular Weight

CAS Number

Synonyms

Application General Coatings Printing/Inks
 Architectural Cosmetic
 Automobile Plastics



RELATIONAL DATABASES

Microtrace LLC

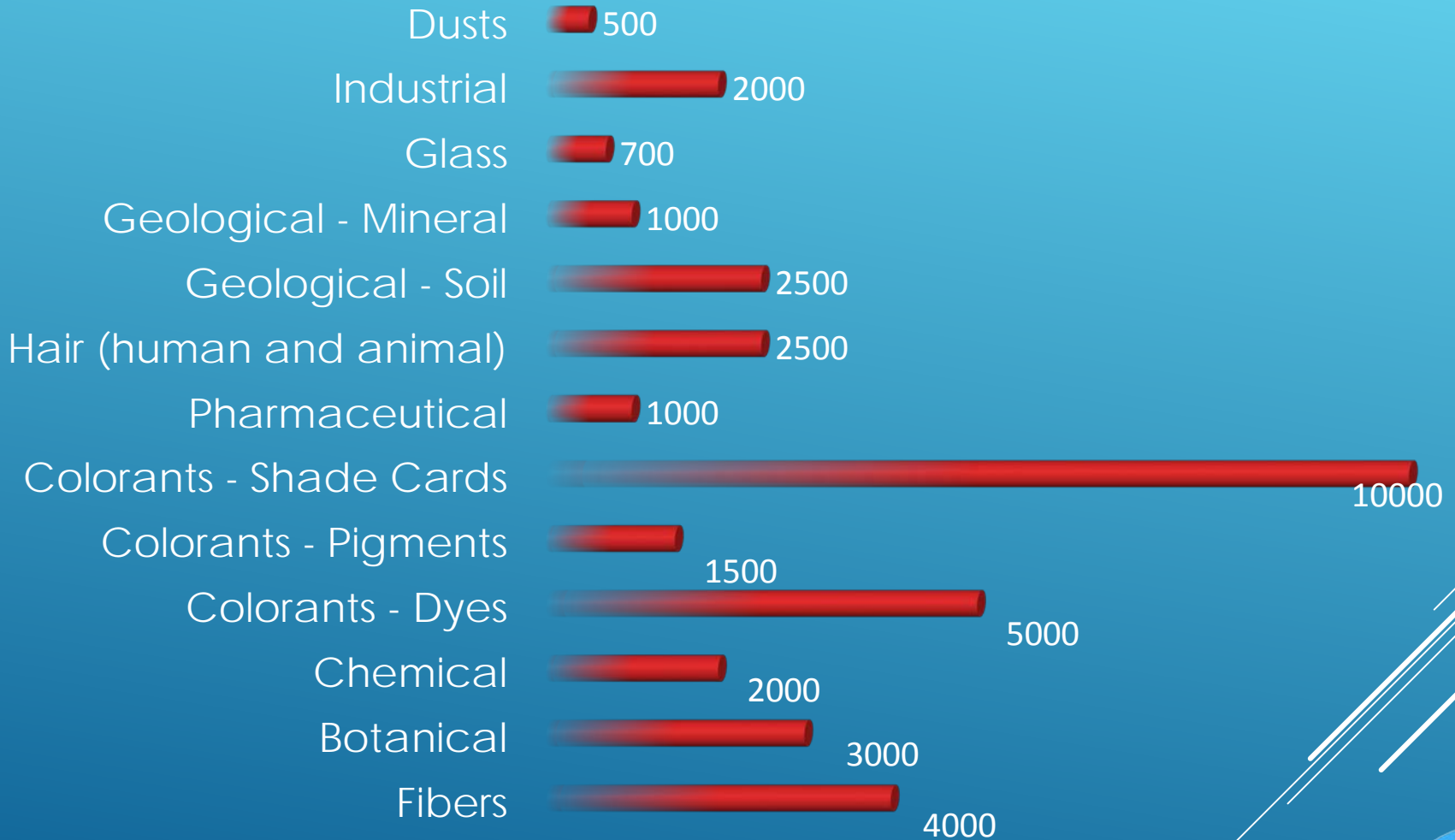
Colorant Database

Physical Samples

Colorant #	Q.I.	Manufacturer	Trade Name	
C-00760	2	Whittaker, Clark, and	Diafil 3590	Go
C-00761	2	Whittaker, Clark, and	Diafil 3525	Go
C-00025	3	Manville	Celite 281	Go
C-00026	3	Whittaker, Clark, and	Silica #9	Go
C-00028	3	Huber Corp.	Zeothix 95	Go
C-00724	3	Whittaker, Clark, and	Silica #19	Go
C-00012	4	Genstart Corp	Manville Celite 289	Go
C-00024	4	Manville	Celite 270	Go
C-00562	4	Cargille	Quartz	Go
C-01156	4	Kremer	Cristobalite (8um)	Go
C-00509	5	Unknown	Celite	Go
C-00751	5	Unknown	Celite	Go



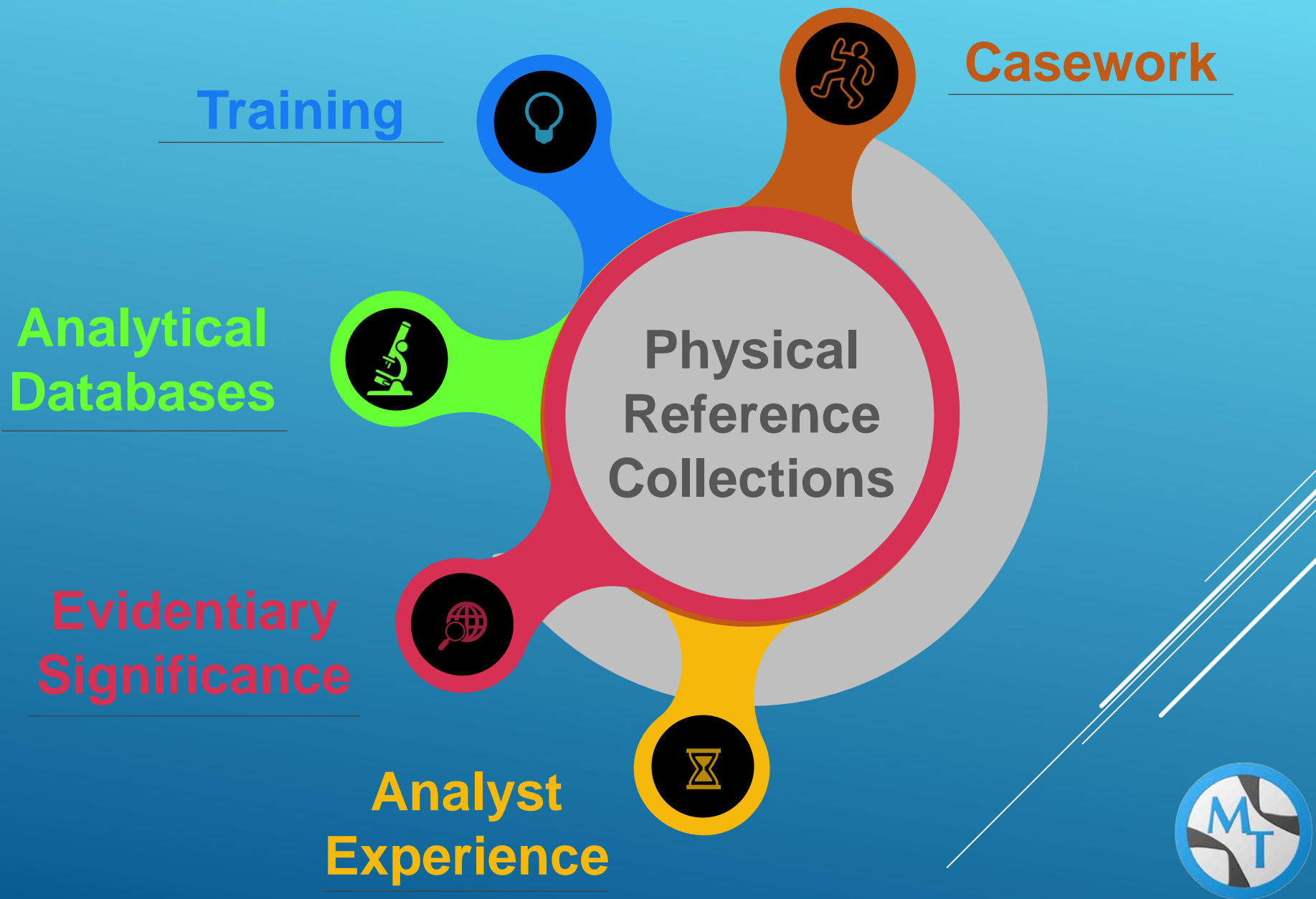
MICROTRACE PHYSICAL COLLECTIONS



Total: ~35k physical reference specimens



ROLE OF COLLECTIONS IN TRACE EVIDENCE



COLLECTION LESSONS



1

Organization & Planning

2

Accepting Inherent Inconsistencies

3

Quality

4

Analytical Data Considerations



QUALITY CONSIDERATIONS

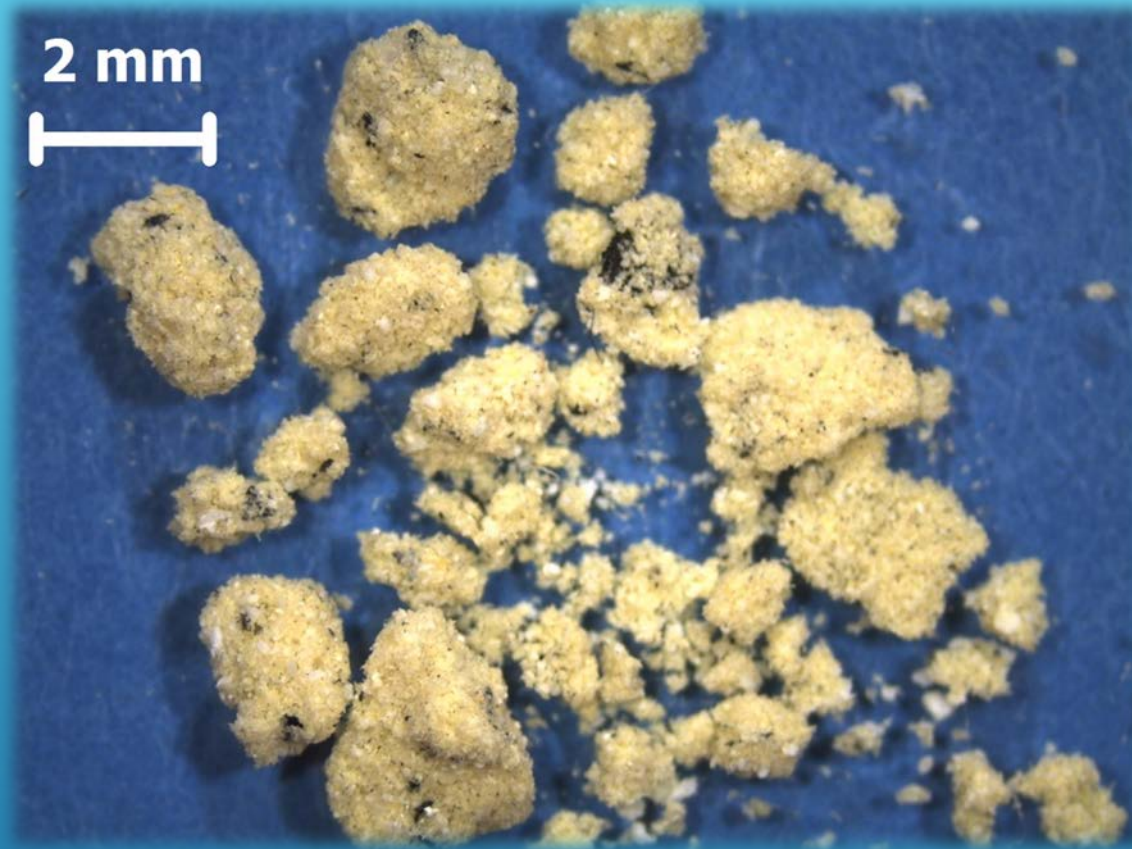
- Audit Logs – to track consistency and trends in data entry
- Quality Considerations - Samples arrive with varying amounts of information
- The concept of a “Quality Index” provides a quick way to estimate the relative value of a sample

Quality Index	Pigment Source	Pigment Name	Authentication Letter	Source	Manufacturer
1	Directly from pigment manufacturer	K	K	K	K
2	Secondary source (e.g., pigment distributor)	K	K	K	K
3	Secondary source	K	U	K	K
3	Secondary source	K	K	U	K
4	Other source	K	U	U	K
5	Other source	K	U	U	U
5	Other source	K	U	K	U

K=Known/On File

U=Unknown

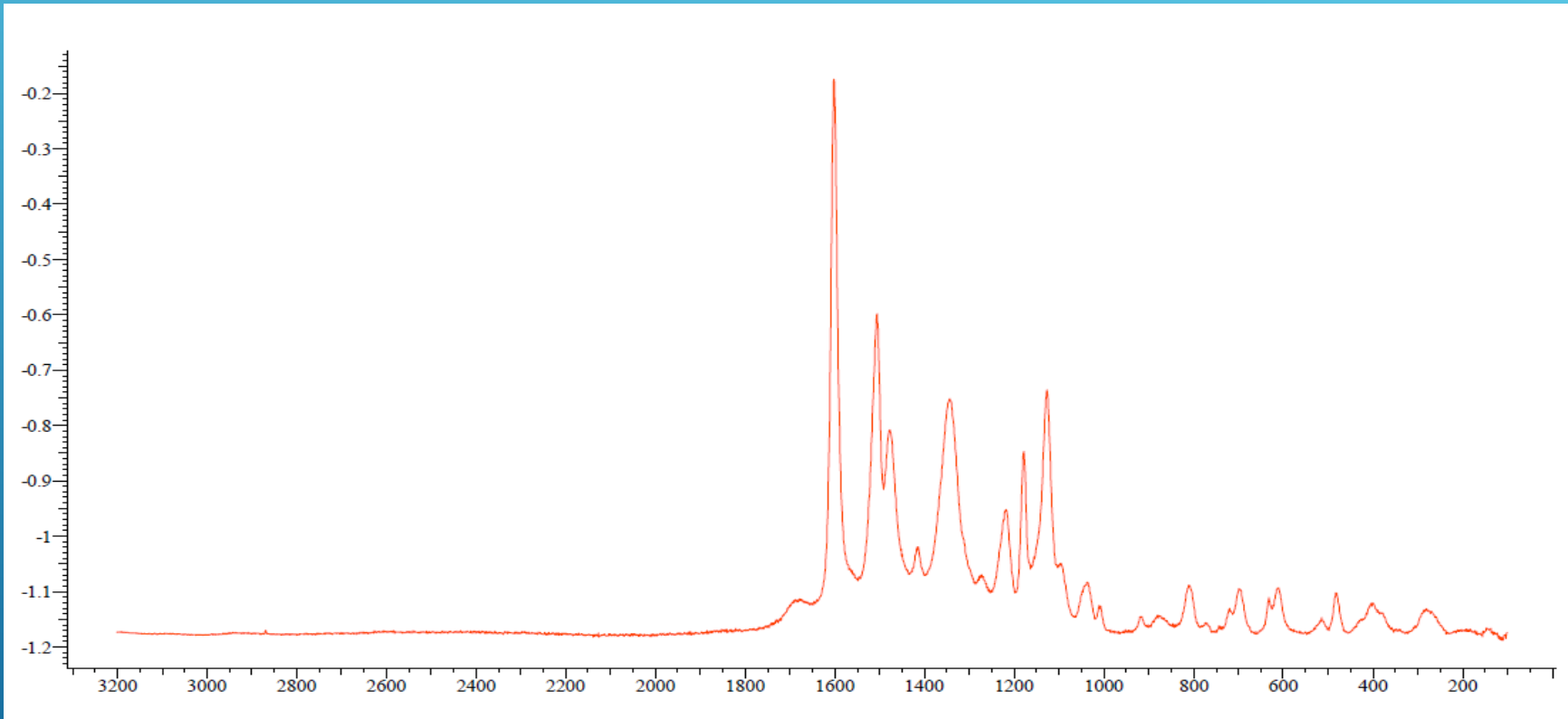




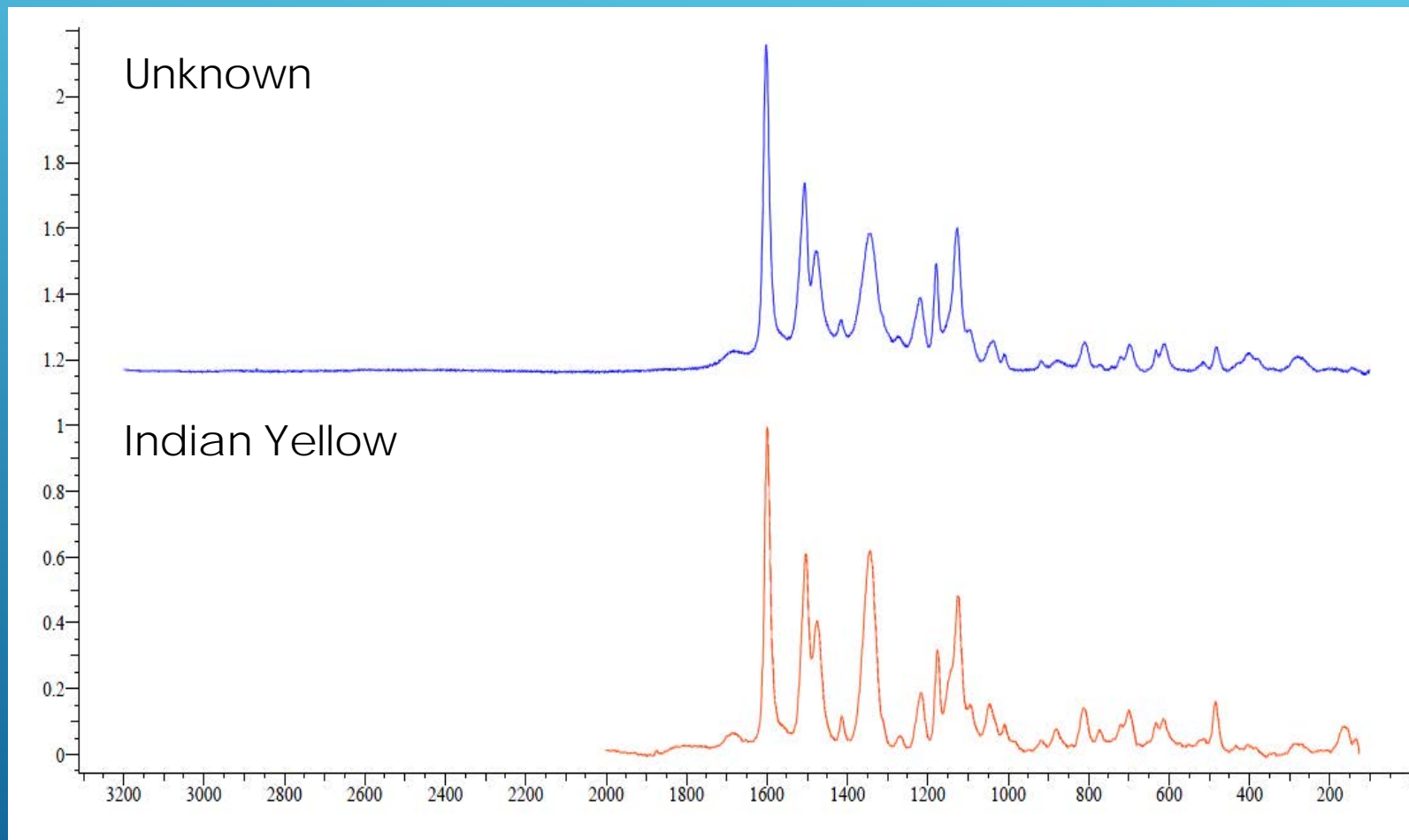
HOW MUCH CAN WE TRUST A
PIGMENT NAME?



RAMAN SPECTRUM OF YELLOW PARTICLE



COMPARISON TO UCL CHEMISTRY LIBRARY

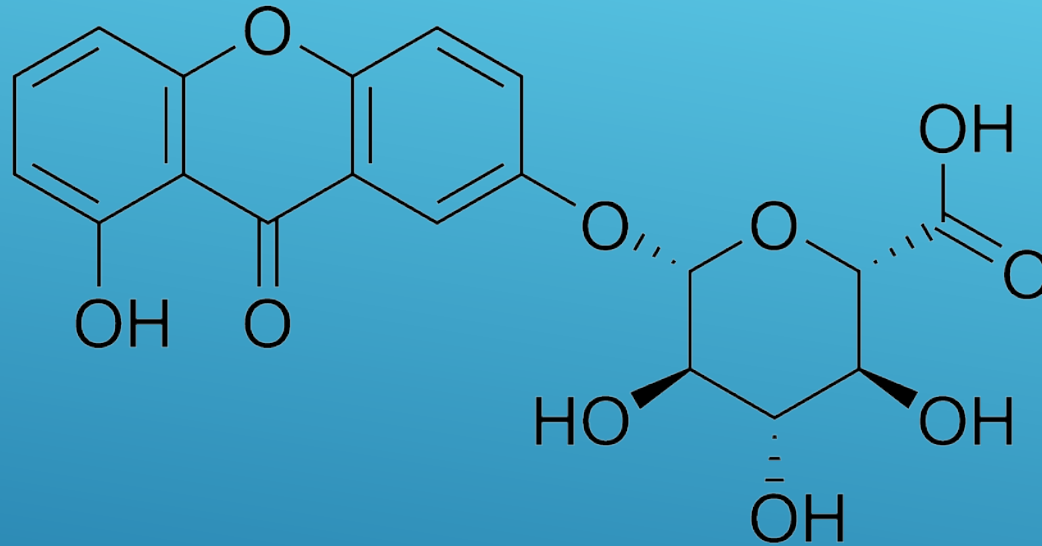


INDIAN YELLOW

- ▶ Produced in India
 - ▶ Likely introduced to India from Persia in the fifteenth century
 - ▶ Common in Mughal period (late 16th to 19th centuries)
- ▶ First confirmed European use by English and Dutch painters in the late 18th century although potentially used as early as 1829
- ▶ True Indian Yellow originated from the urine of cows fed on a diet of Mango leaves
- ▶ Quickly fell out of practice due to the resulting odor, health issues with cows, and the general difficulty of preparation



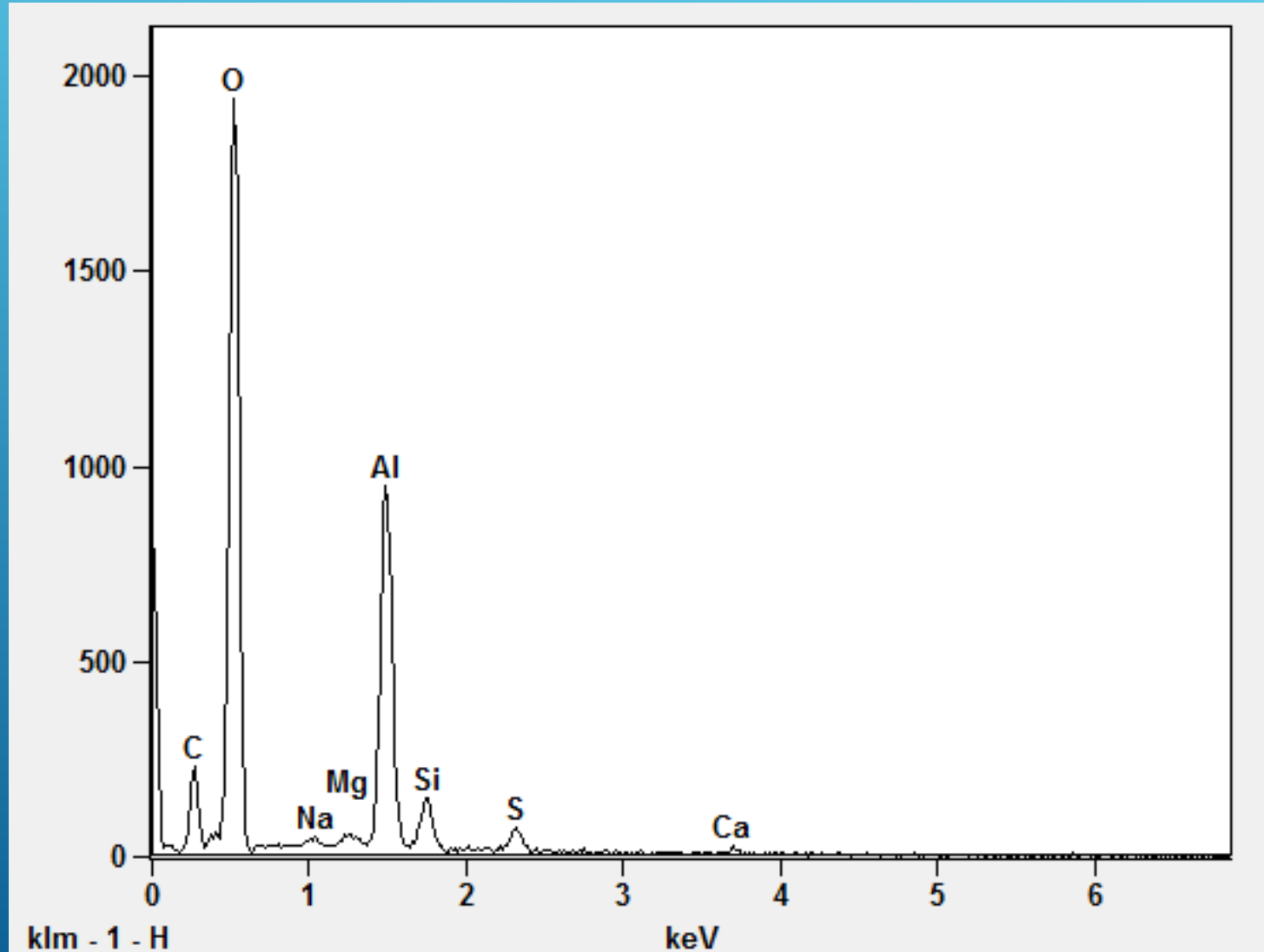
CHEMICAL COMPOSITION



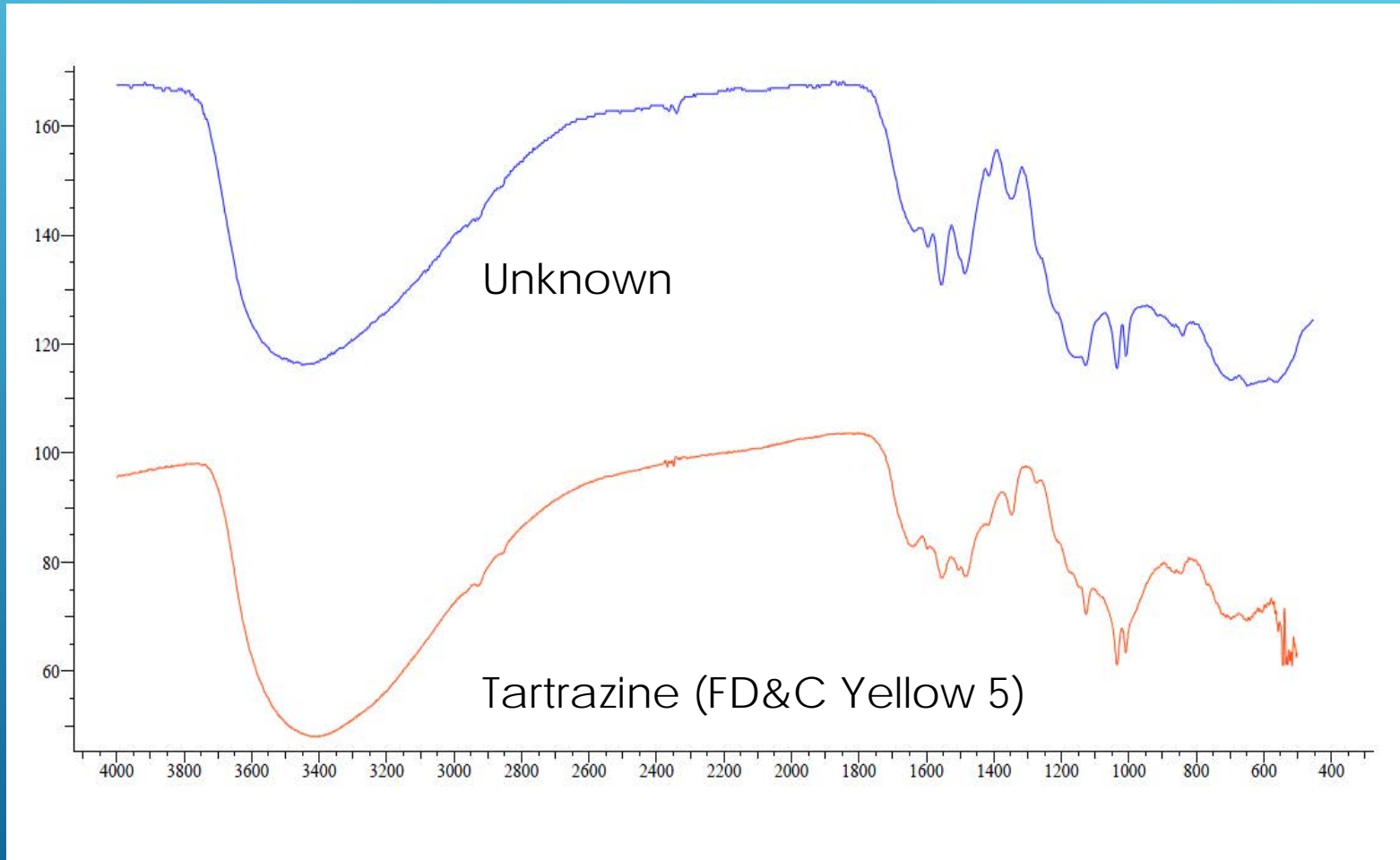
Magnesium and/or calcium salts of euxanthic acid
($C_{19}H_{16}O_{11}Mg \cdot 5H_2O$)



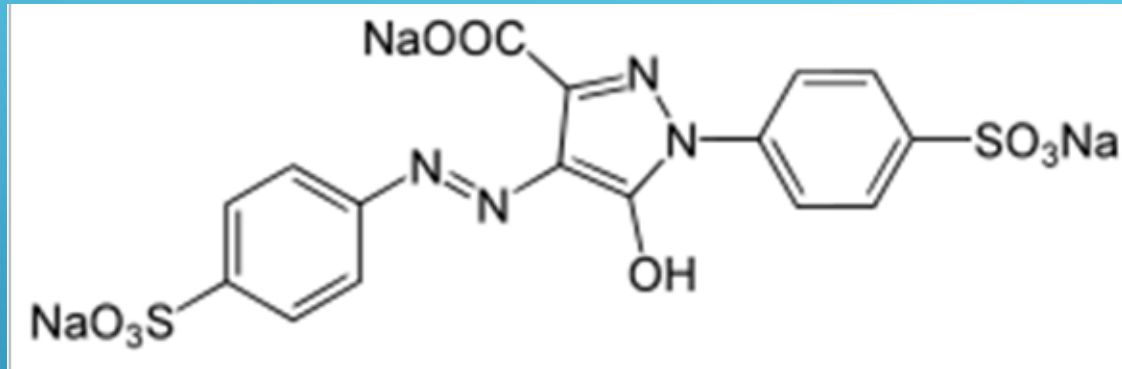
INCONSISTENCIES



FTIR INCONSISTENCIES



FD & C YELLOW #5

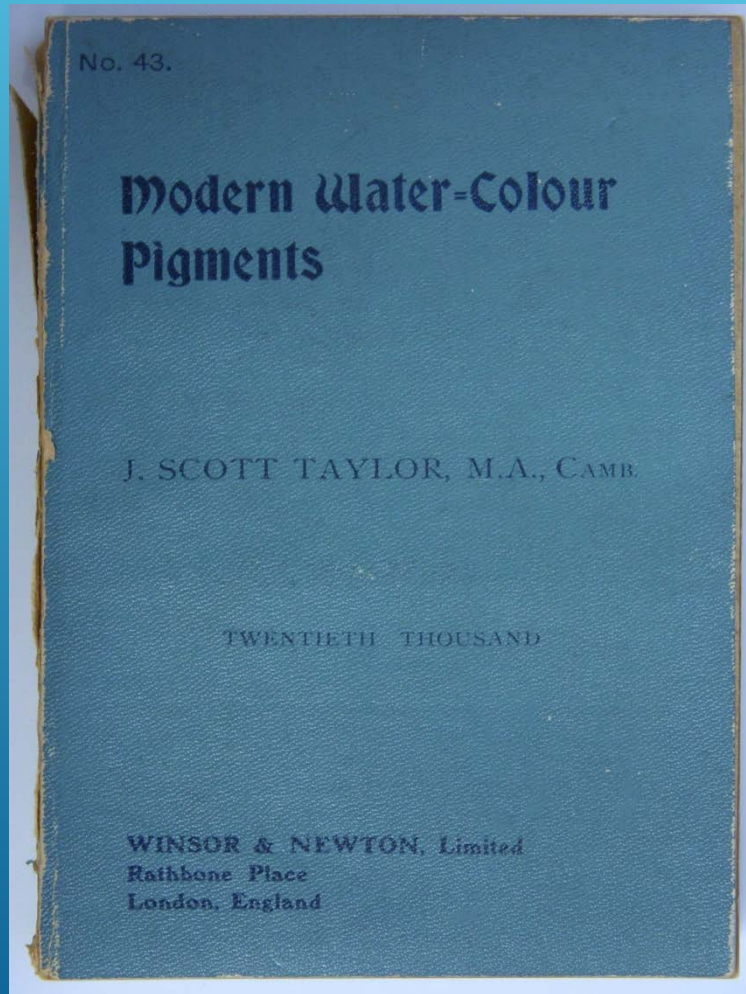


▶ Tartrazine

- ▶ Synthetic azo dye used as a colorant in foods, cosmetics and pharmaceuticals
- ▶ Commonly used as a lake pigment



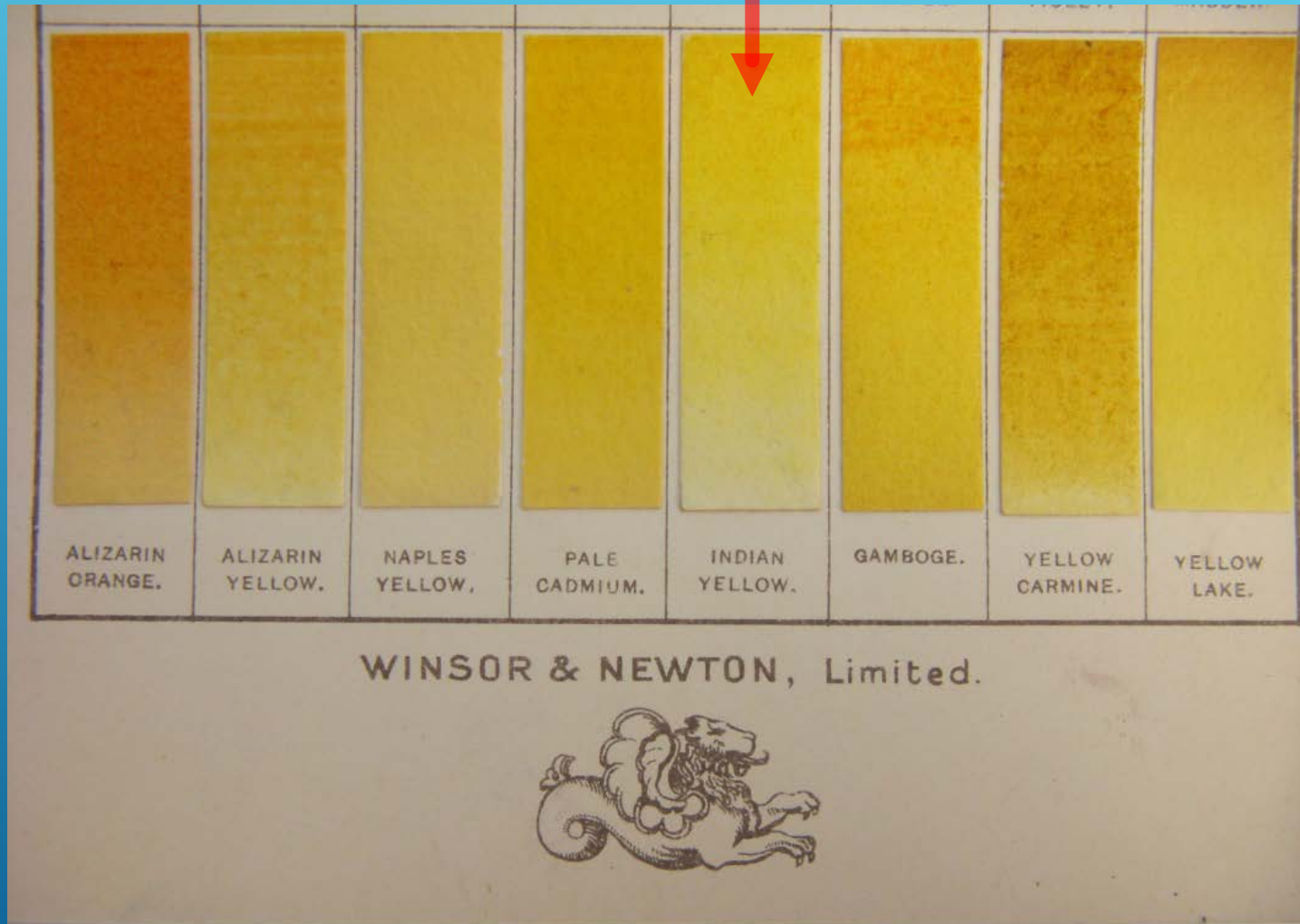
MICROTRACE PHYSICAL REFERENCE SAMPLES



1. Winsor & Newton Vial (Undated)
2. Rowney Vial (Undated)
3. Winsor & Newton book (1887) containing water-colored cards. States camel urine as source.



WINSOR & NEWTON BOOK

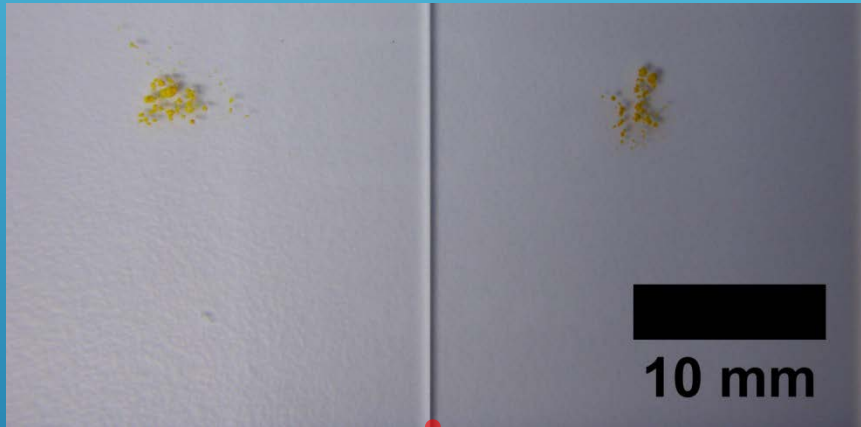


FLUORESCENCE

White light

1. W & N

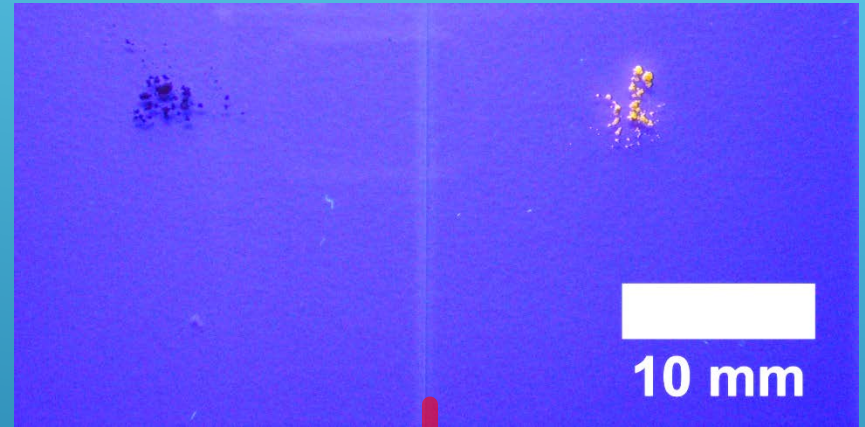
2. Rowney



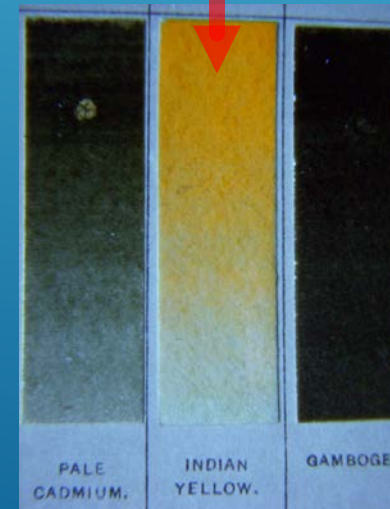
UV light

1. W & N

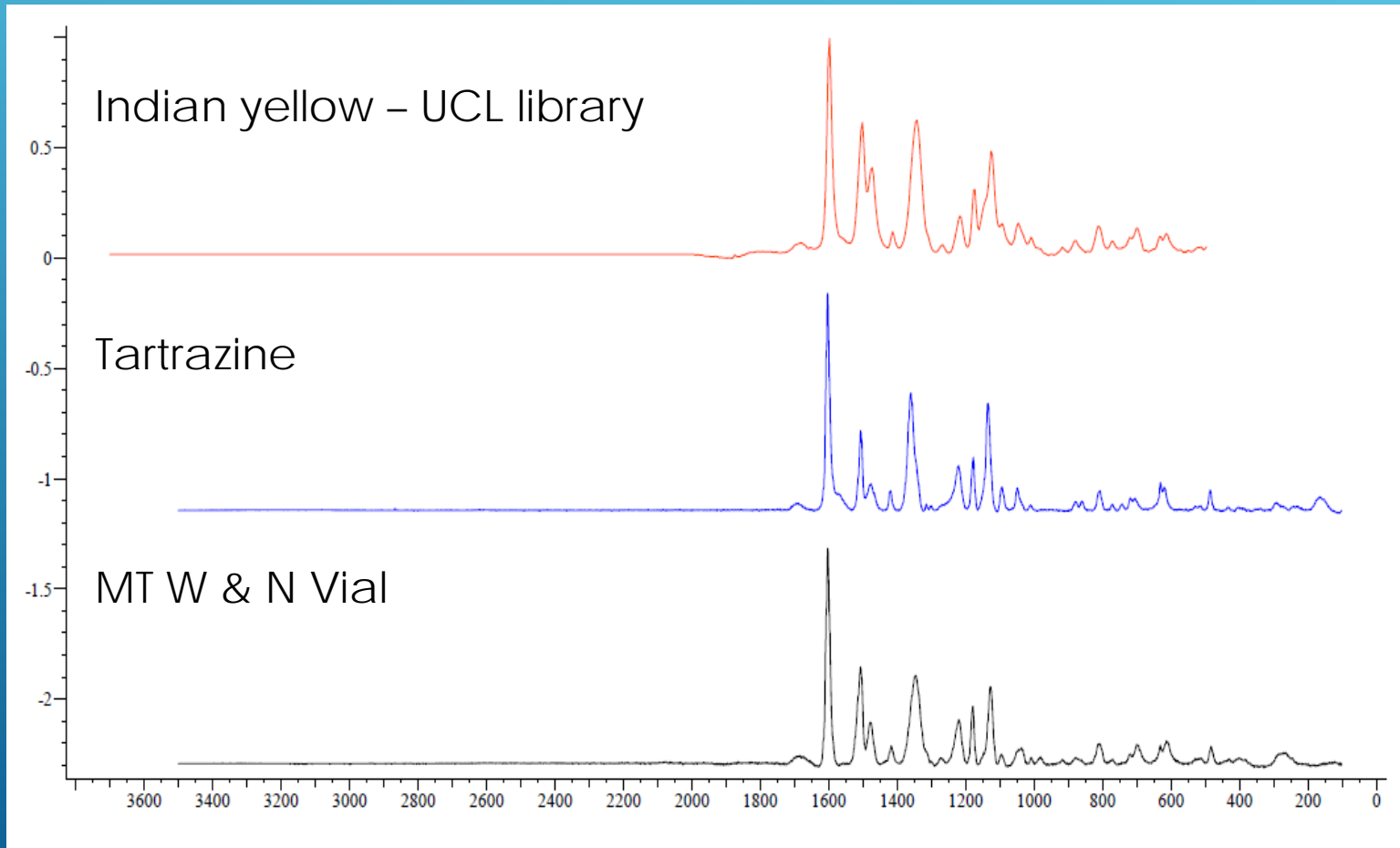
2. Rowney



3. W & N



RAMAN: REFERENCE SPECTRA



XRD PEAKS FROM ROWNEY SAMPLE

2-Theta			
9.164	19.102	25.642	34.679
9.78	20.119	26.7	36.04
11.722	20.358	27.279	36.5
12.679	20.859	27.578	37.401
13.339	21.958	28.478	38.779
15.258	22.142	29.466	40.14
16.142	22.877	29.94	42.764
17.02	23.5	31.787	43.359
17.536	23.742	32.316	43.764
18.46	25.283	33.32	46.041

Indian yellow

Lead chromate

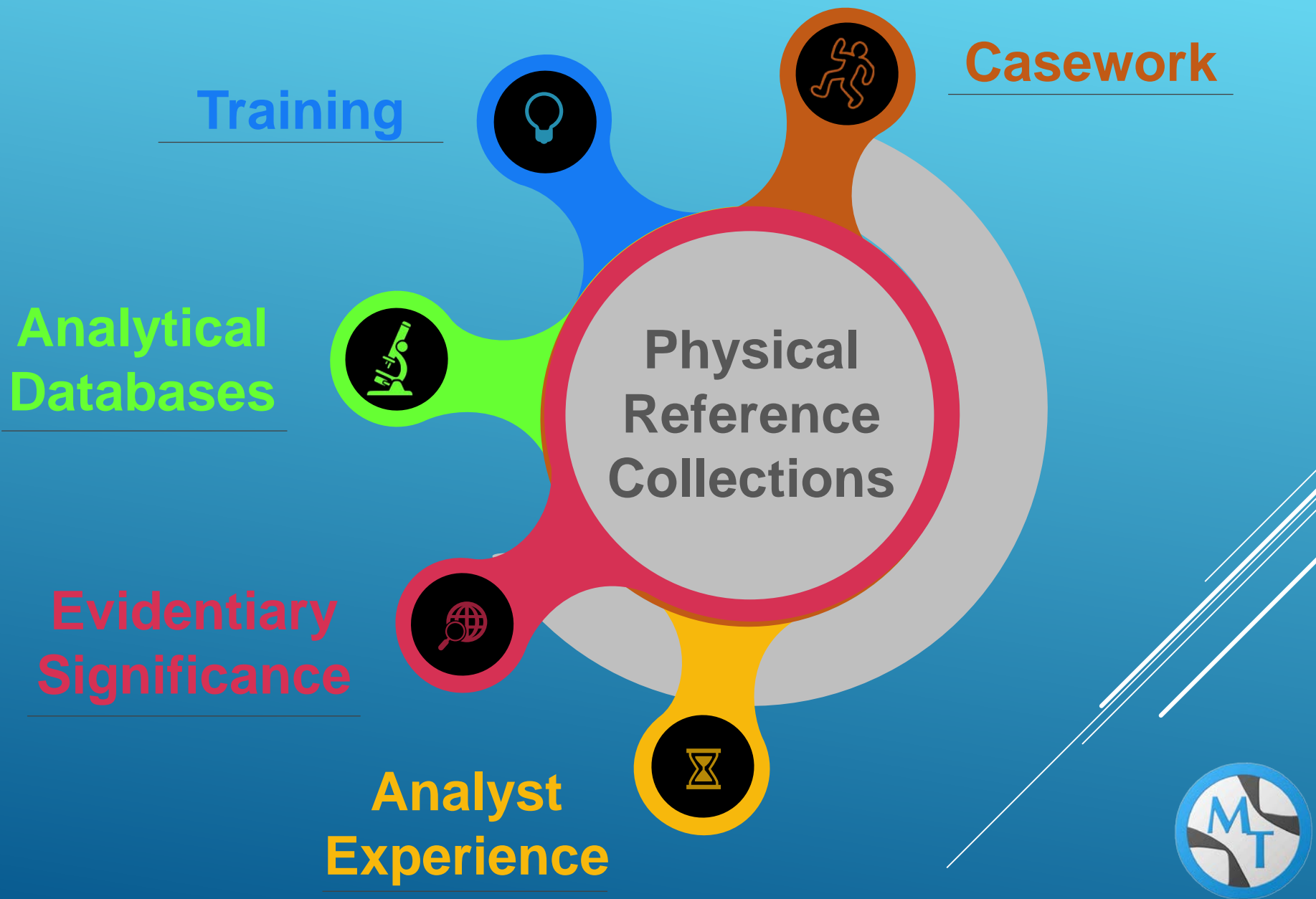
Indian Yellow and lead chromate

CONCLUSIONS

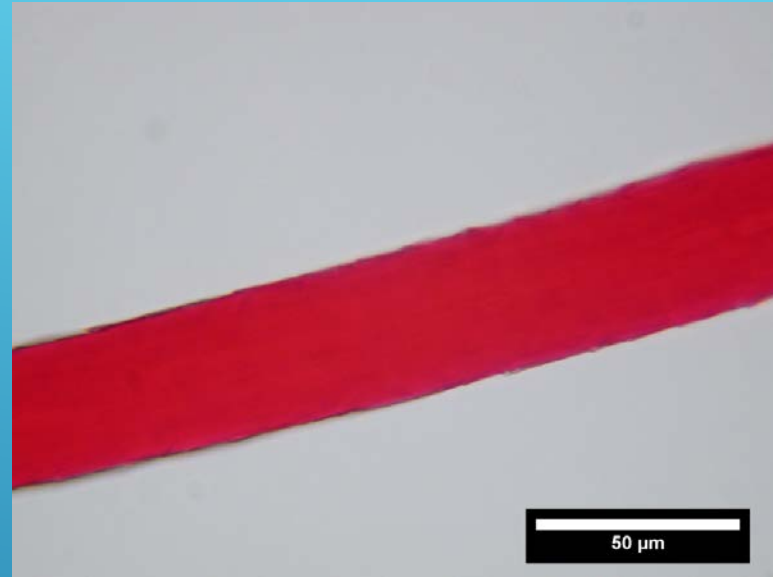
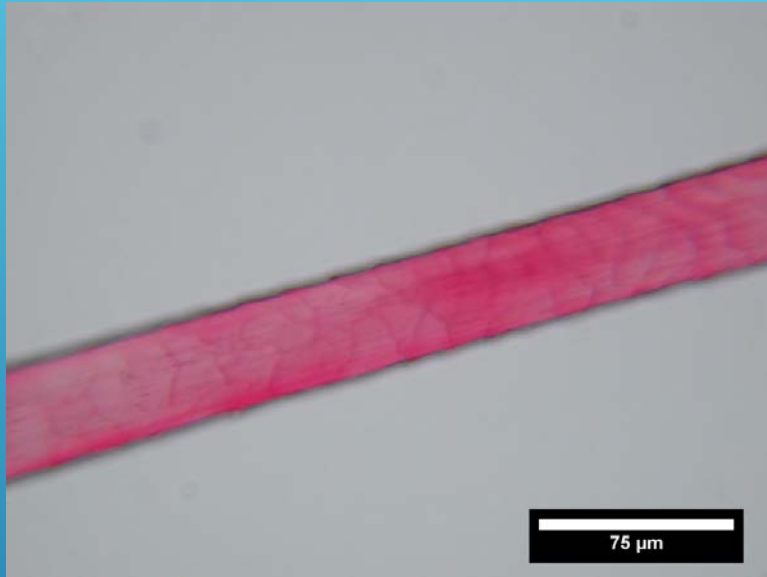
- ▶ 1. Windsor & Newton pigment (vial)
 - ▶ Tartrazine
- ▶ 2. Rowney pigment (vial)
 - ▶ Indian Yellow and Lead chromate mixture
- ▶ 3. Windsor & Newton Book
 - ▶ True Indian yellow
- ▶ 4. UCL Reference Spectrum labeled "Indian Yellow"
 - ▶ Tartrazine
- ▶ Unknown Sample
 - ▶ Tartrazine

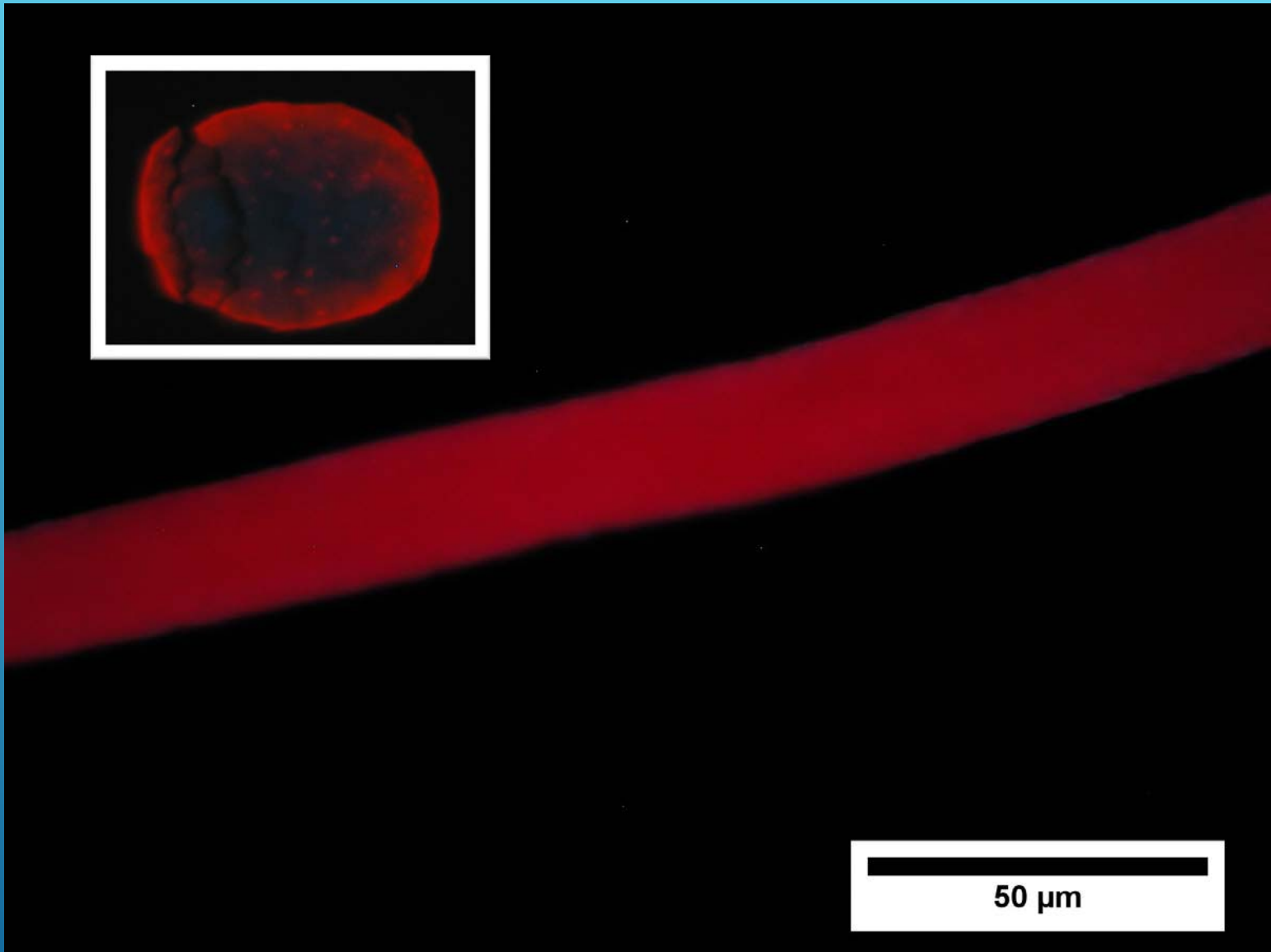


ROLE OF COLLECTIONS IN TRACE EVIDENCE



EXAMPLE – FULL DYE IDENTIFICATION



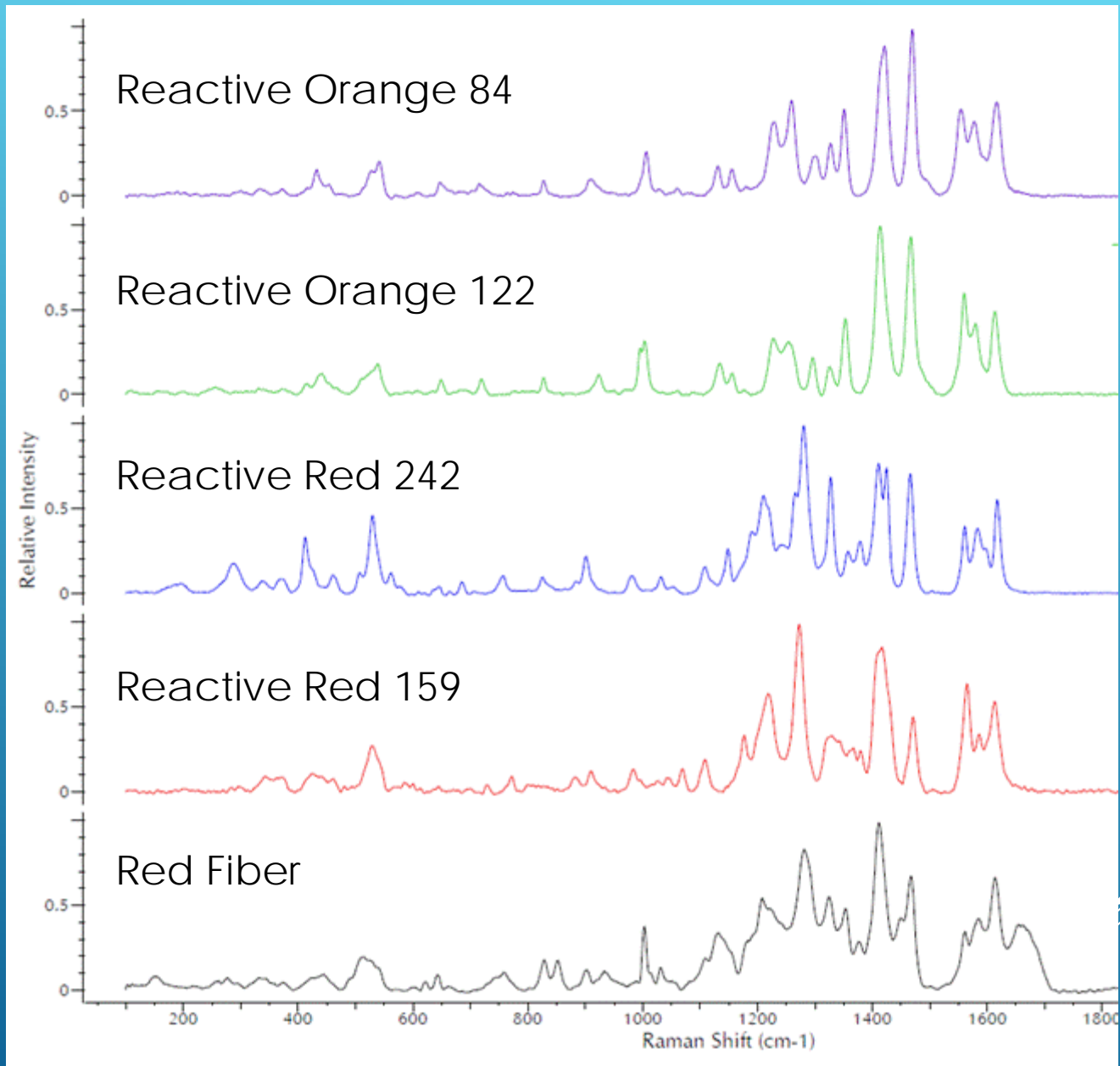


Ultraviolet excitation

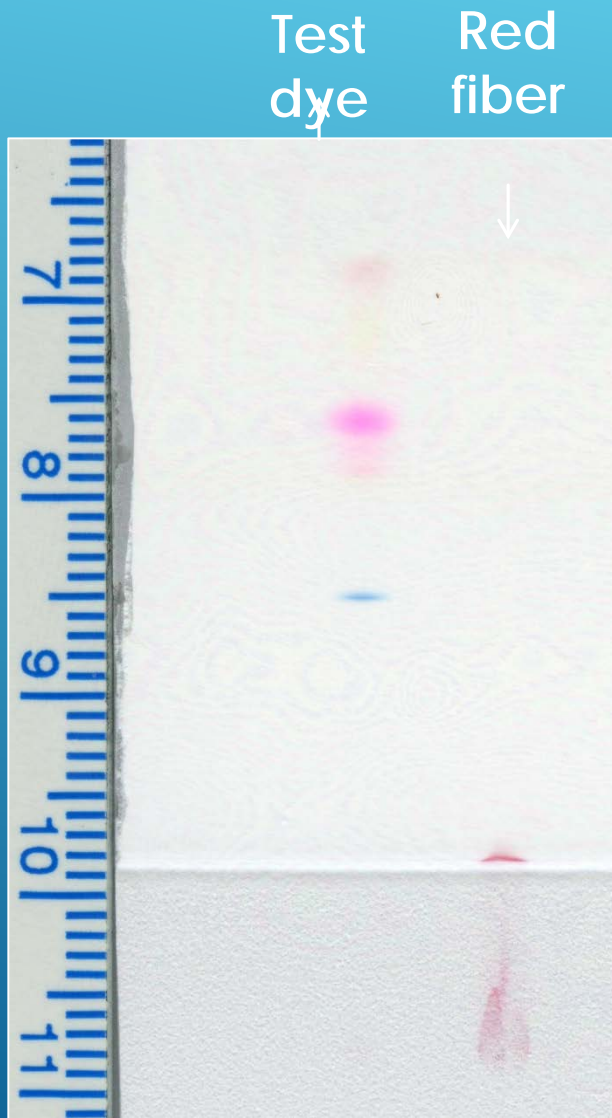


Raman Spectrum

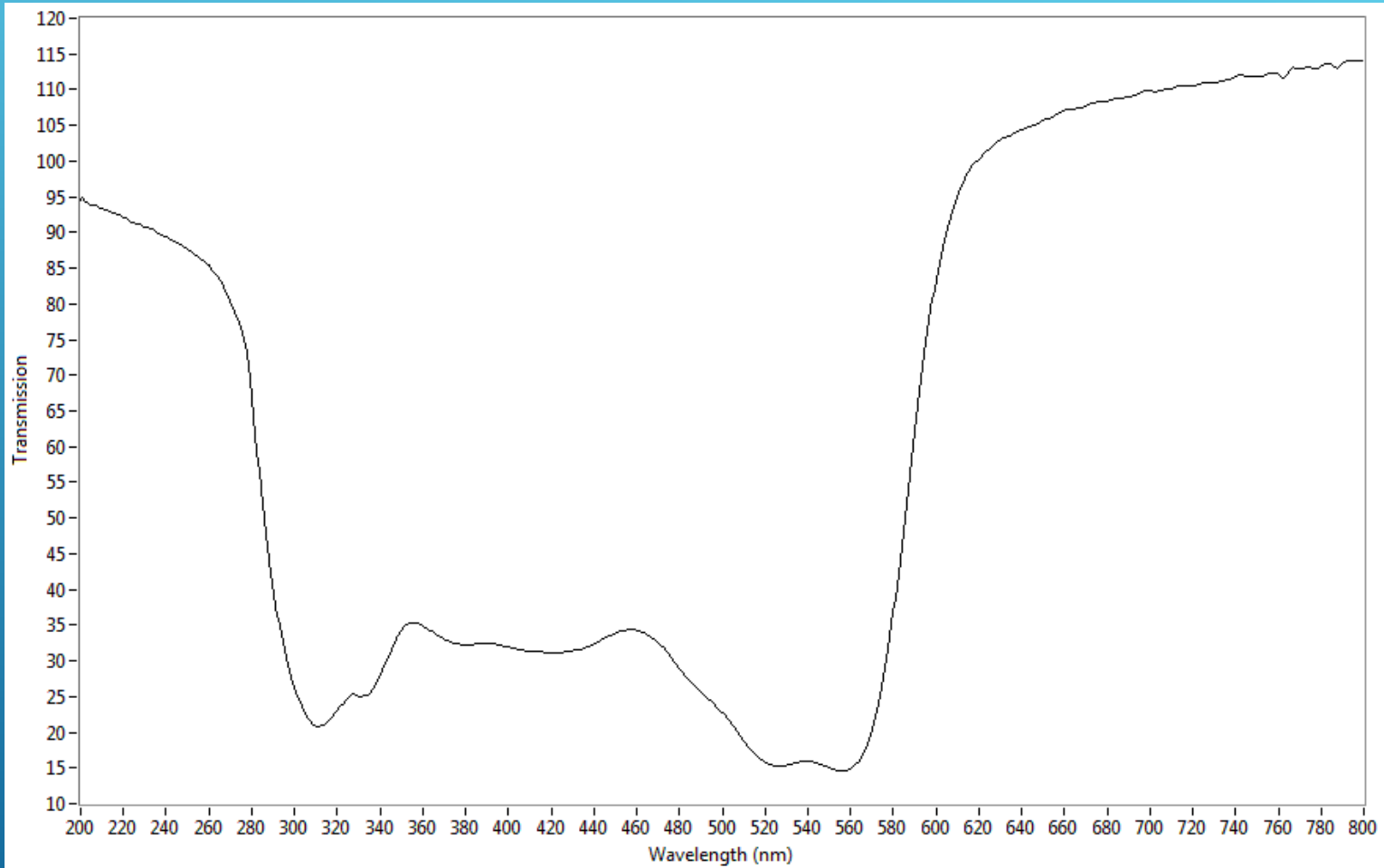




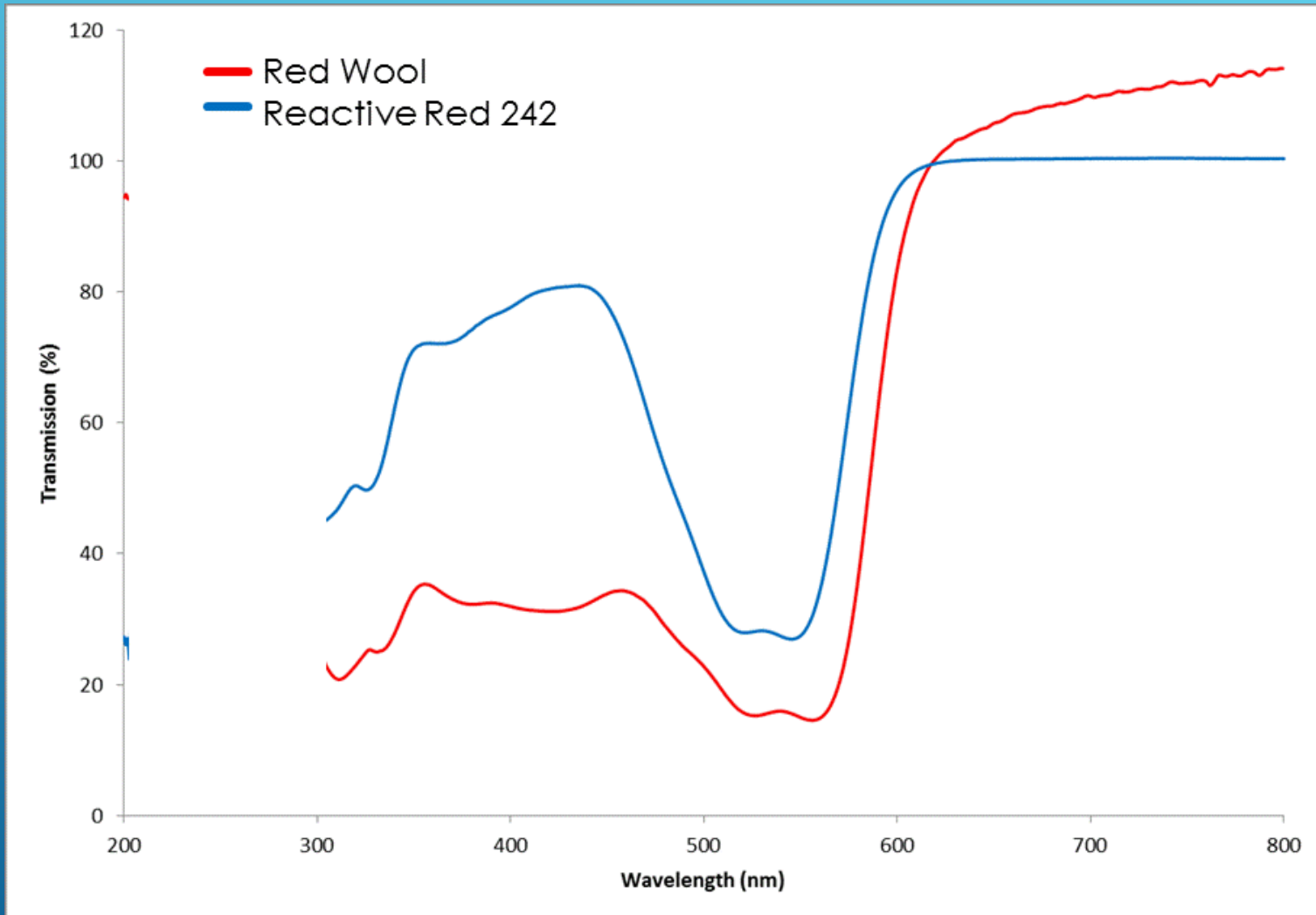
TLC



MSP



MSP



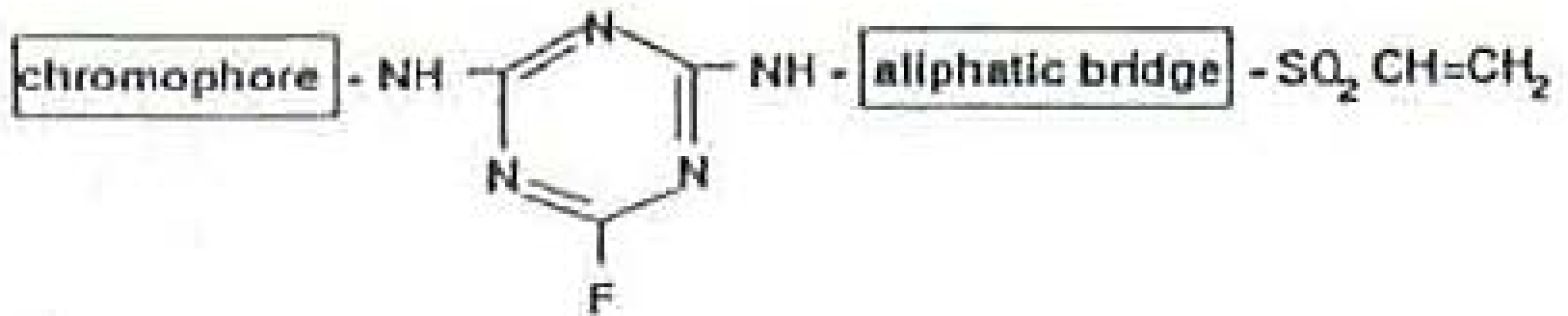


Fig. 1. Structure of a Cibacron C dye containing a fluorotriazine and a vinyl sulfone group.

CIBACRON DYE - GENERAL STRUCTURE



Shade Cards

Cibacron Rot C-R Rouge Cibacrone C-R Cibacron Red C-R

ciba

Basiselement für Kombinationsfärbungen mit guten Peroxid- und Chlor-
echtheiten, vor allem im Pad-Batch- und Auszieh-Verfahren.

Élément de base pour des teintures composées dotées de bonnes solidités
au peroxyde et au chlore, surtout en teinture pad-batch et par épuisement.

Basis for combination shades with good fastness to peroxide and chlorine,
particularly in the pad-batch and exhaust methods.

Verhalten / Eignung Comportement / aptitude Behaviour / Suitability

- sehr gut / très bon(ne) / very good
- ▲ gut / bon(ne) / good
- mäßig / moyen(ne) / moderate
- nicht empfohlen / pas recommandé / not recommended

	Pad-Batch	Pad-Dry/Pad-Steam	Pad-Steam	Pad-Thermofix	Kurzflotte/boil court/ short liquor
Färbeverfahren Procédé de teinture Dyeing process	■	-	-	-	■
Decken later Baumwolle Couverture du coton mort Coverage of dead cotton	□	-	-	-	□
Ausgleich streifigfärbender Viskose Couverture de la viscose barrée Coverage of barry viscose	□	-	-	-	□
Ton-in-Ton-Färbung Teinture ton sur ton Solid dyeing	CO/CP (50:50)	■	-	-	□
Kunstlicht Lumière artificielle Artificial light					G
Thermosal-Beständigkeit Stabilité au thermosolage Stability to thermosoling		CO	■		
HT-Überfärben Sureinture à HT HT cross-dyeing		CO	■		
Ätzbarkeit Rongeabilité Dischargeability	CO	neutral / neutre bis / jusqu'à / up to RT/SD			1/6
Reduktionsbeständigkeit Stabilité à la réduction Stability to reduction					■
Aufhellen / Abziehen Eclaircissement / Démontage Shade weakening / Stripping	Method(e)	O	AB	E	
		65%	■	□	
Nachbleiche Postblanchiment Post bleaching					■
Auswaschbarkeit Lavabilité Washing-off					■

CO merc.



Pad-Batch C-55295 2.4 g/kg



Pad-Batch C-55296 12 g/kg



Pad-Batch C-55297 24 g/kg

CO gebleicht / blanchi / bleached



Pad-Batch C-55298 3.6 g/kg
Kurzflotte / b. court / short liquor 0.4%



Pad-Batch C-55299 3.6 g/kg
Kurzflotte / b. court / short liquor 3.8%

3480

CO merc.



Pad-Batch C-55295 2.4 g/kg



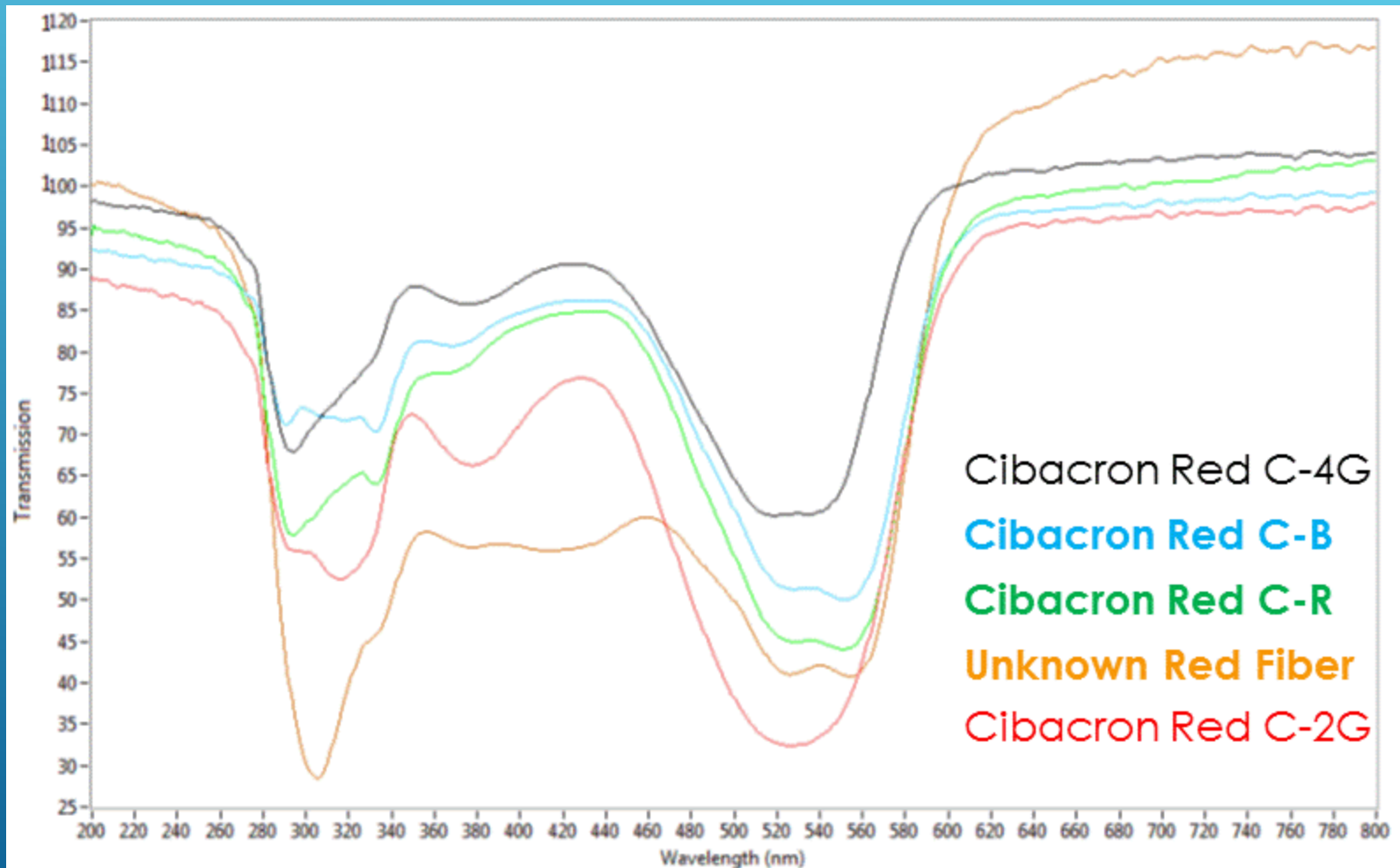
Pad-Batch C-55296 12 g/kg



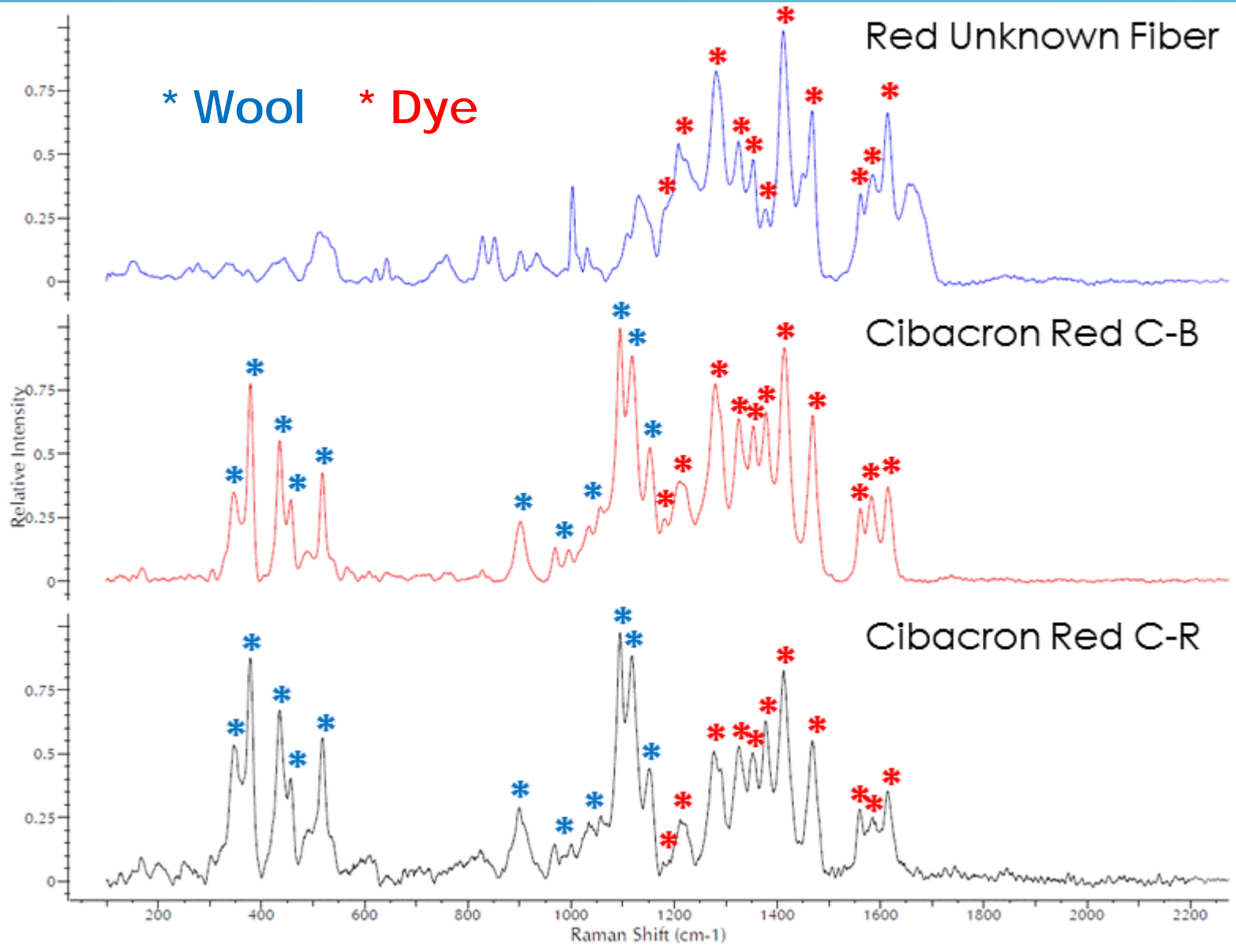
Pad-Batch C-55297 24 g/kg



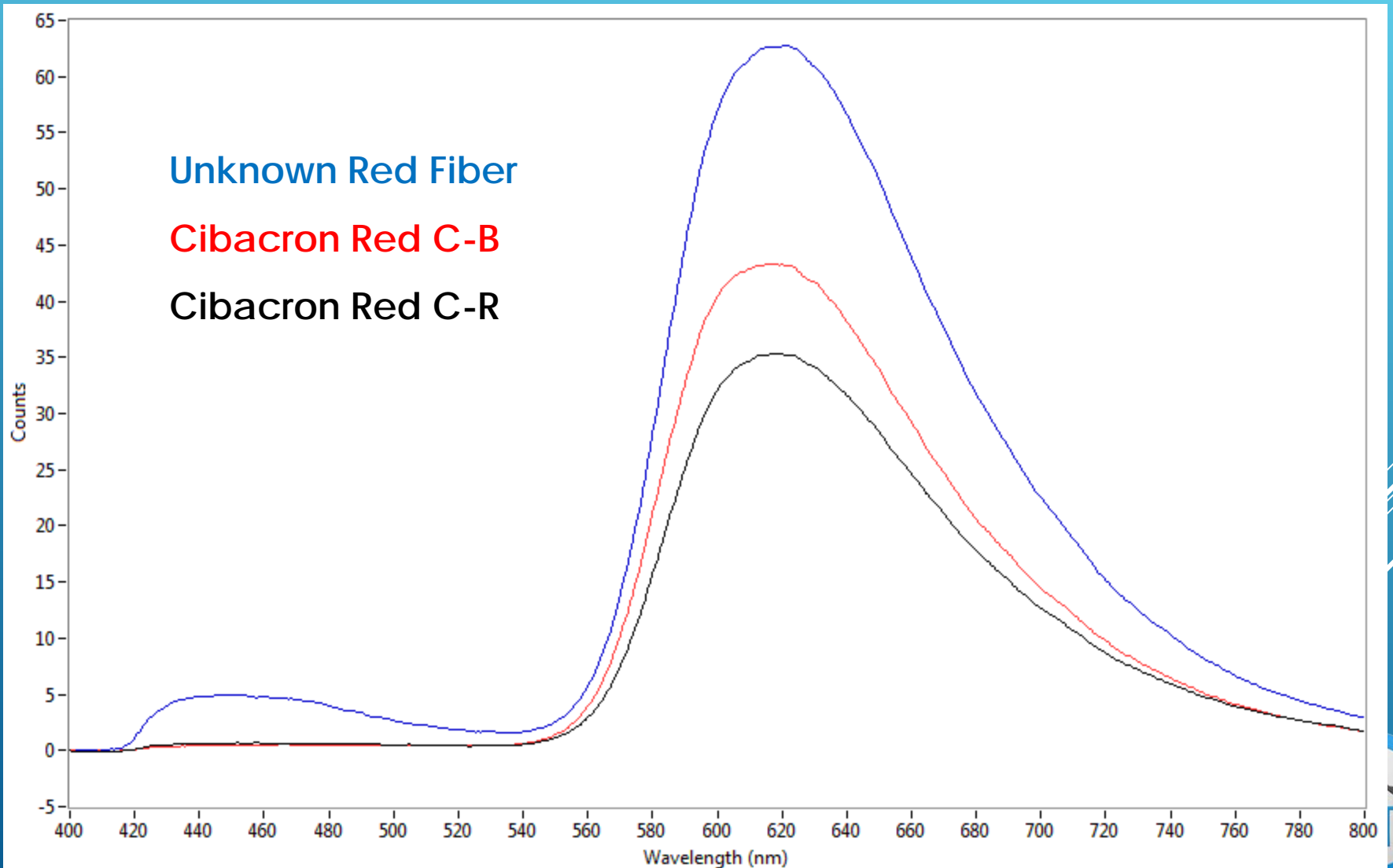
MSP of Cibacron Dyes



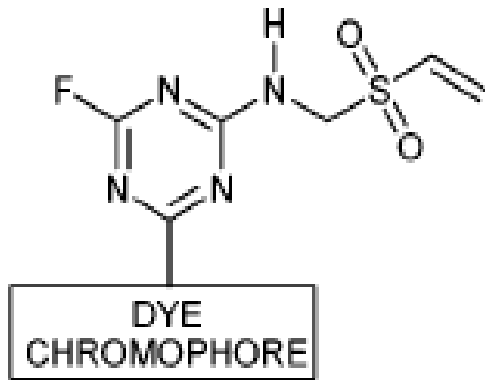
Raman of Cibacron Dyes



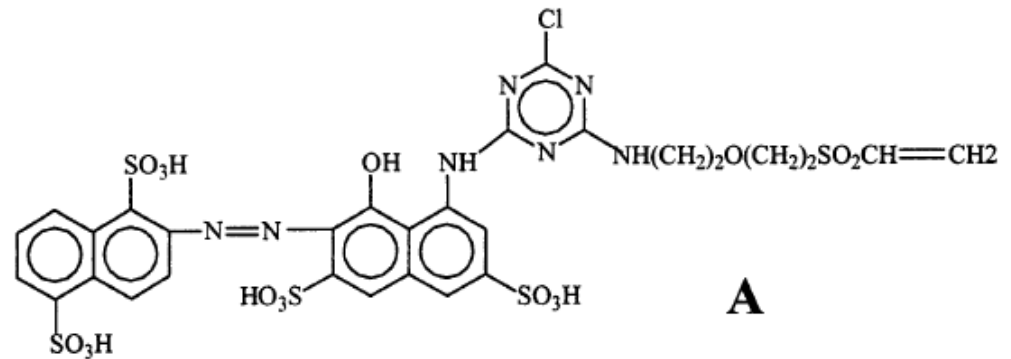
Fluorescence Emission



CANDIDATE STRUCTURES



Cibacron Red C-R
(C.I. Reactive Red 238)



Cibacron Red C-B
(C.I. Reactive Red 235)

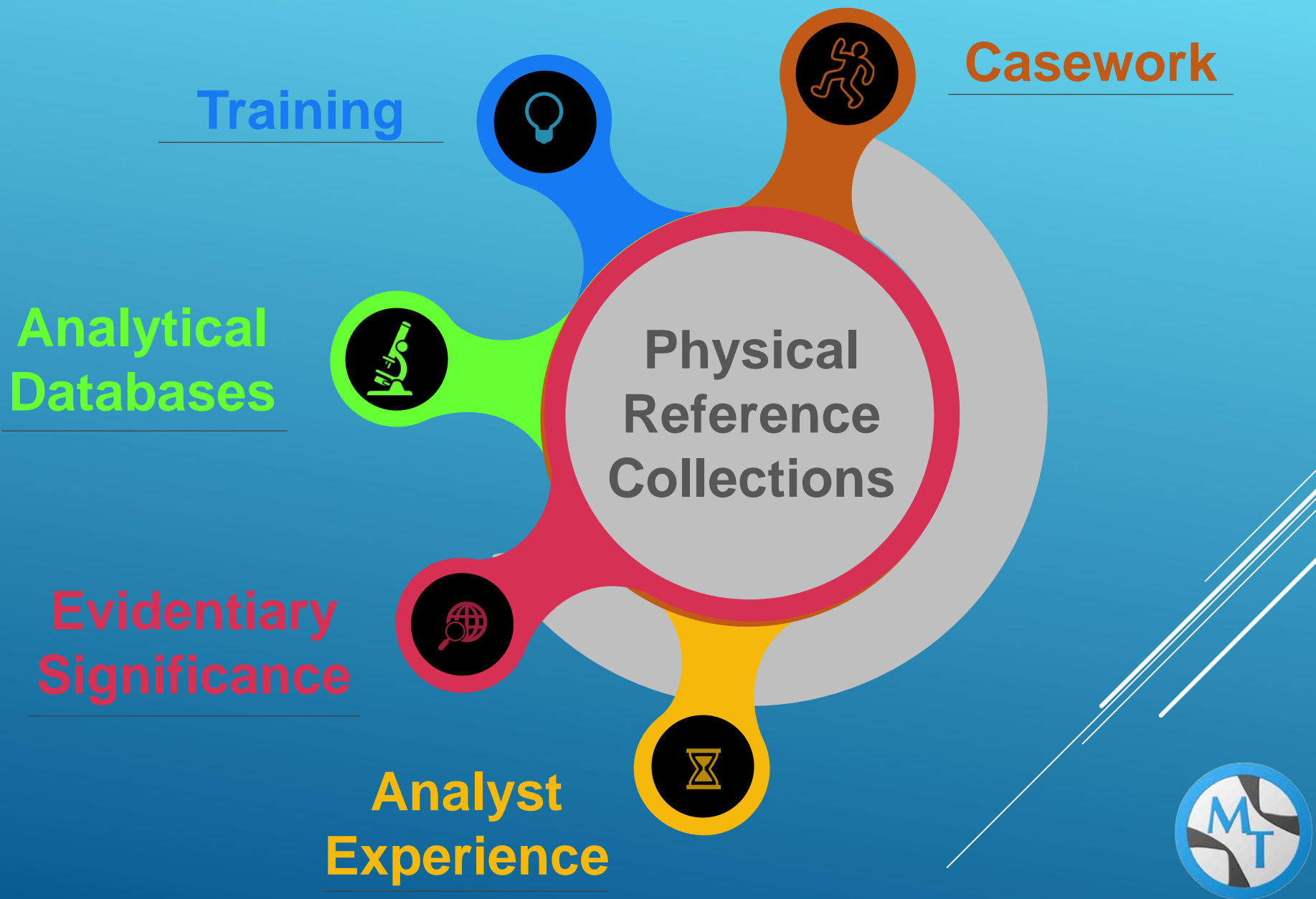


ANALYTICAL PATH

- ▶ **Likely dye class identified:** Raman spectral database show sample with similarities but no matching reference spectra.
- ▶ **Likely chromophore identified:** MSP spectral comparison to MSP reference spectra suggests Reactive Red 242 but Raman spectrum doesn't match.
- ▶ **Literature search for chromophore:** AATCC article suggests Bi-reactive Cibacron Class, consistent with EDS.
- ▶ **Reference samples from Shade Cards:** Data from several reference Cibacron dyes on fibers in our physical reference collection (shade cards_ suggests two candidate dyes (differ by halogen)
- ▶ **Concentration Calculation:** Shade cards were used to produce a calibration curve and the calculate dye concentration on wool fiber (~1.5%).



ROLE OF COLLECTIONS IN TRACE EVIDENCE



THANK YOU

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