Surface Enhanced Raman Spectroscopy (SERS) and Databases for the Characterization of Dyes

Deanna O'Donnell, Ph.D.

Trace Evidence Symposium

Kansas City, Missouri

August 11th, 2011

The following research was conducted at

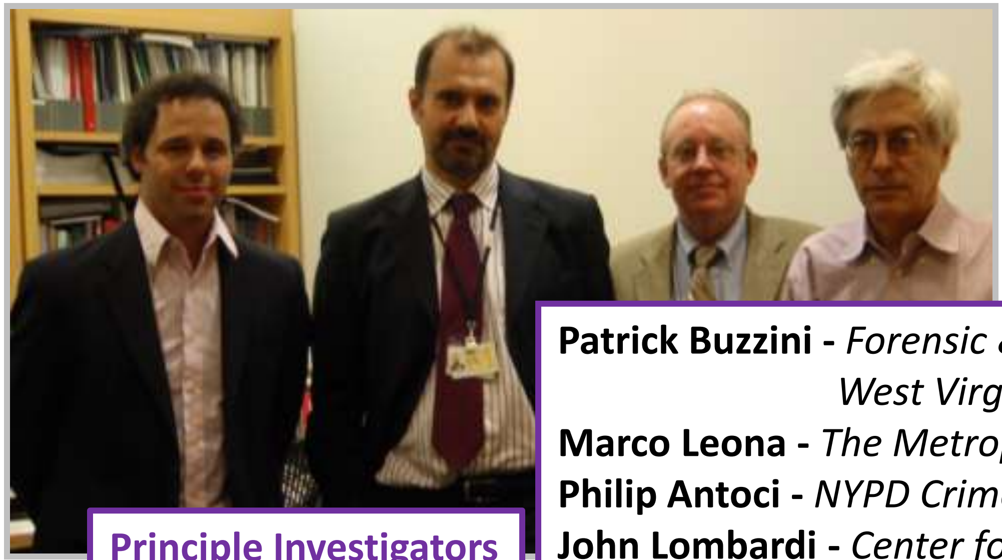
City College of New York

Metropolitan Museum of Art

New York, NY

Research Objectives

- To validate SERS in a forensic context, and show the conditions under which Raman spectroscopy and especially SERS contribute to the value of forensic science.
- To compare both SERS and normal Raman spectra, and to explore the conditions in which each may be of value.
- To validate certain specialized SERS techniques
- To provide useful protocols for use of field workers
- To provide a searchable database for rapid and reliable field use.



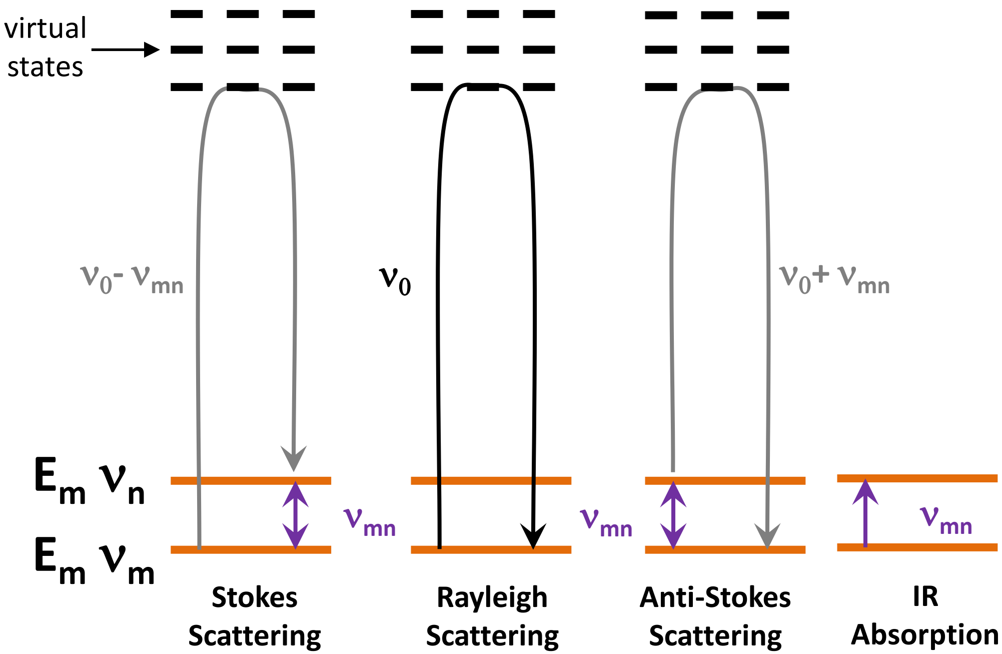
Principle Investigators (*left to right*):

Patrick Buzzini - *Forensic & Investigative Science Program, West Virginia University*
Marco Leona - *The Metropolitan Museum of Art, New York*
Philip Antoci - *NYPD Crime Laboratory*
John Lombardi - *Center for the Analysis of Structures and Interfaces, City College of New York*

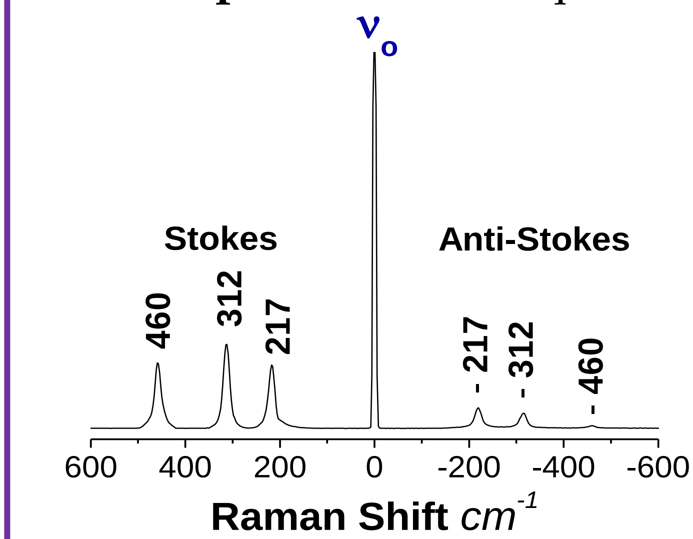
Why Raman Spectroscopy?

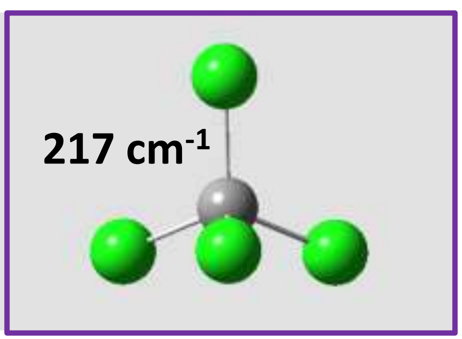
Raman is non-destructive and allows *in-situ* detection

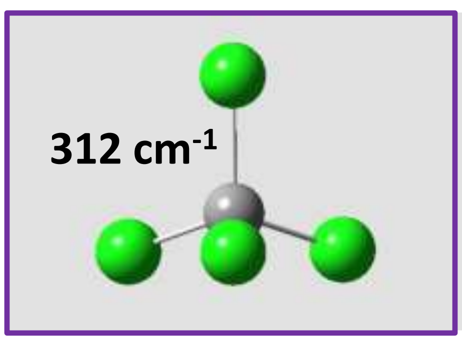
Raman spectra may readily be obtained in aqueous solution (not possible with IR)

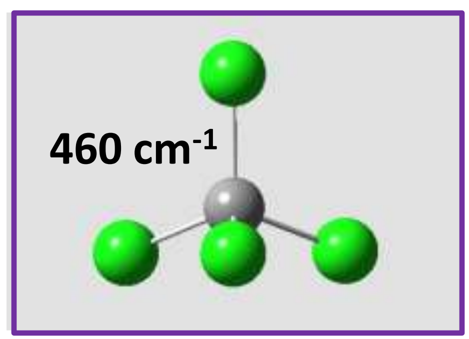


Stokes and Anti-stokes Raman Spectrum of CCl_4





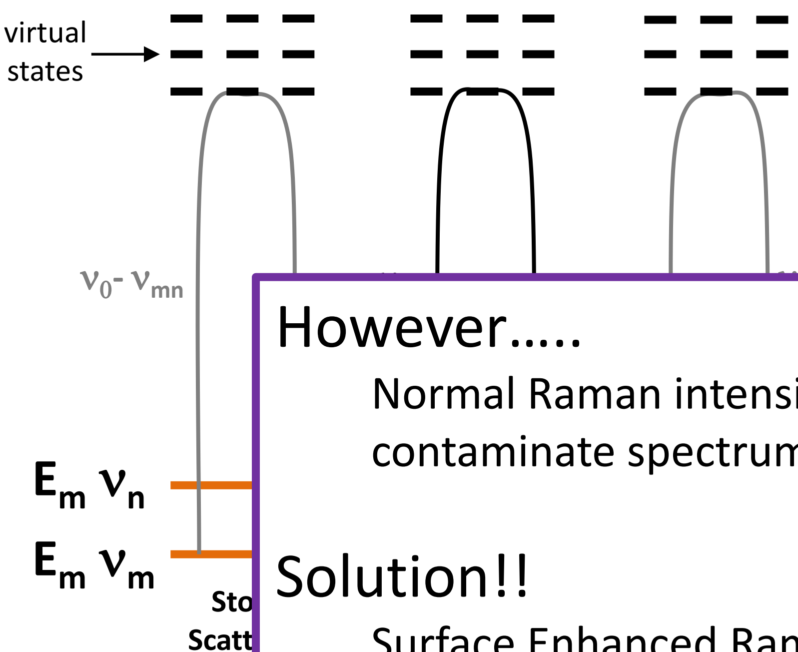


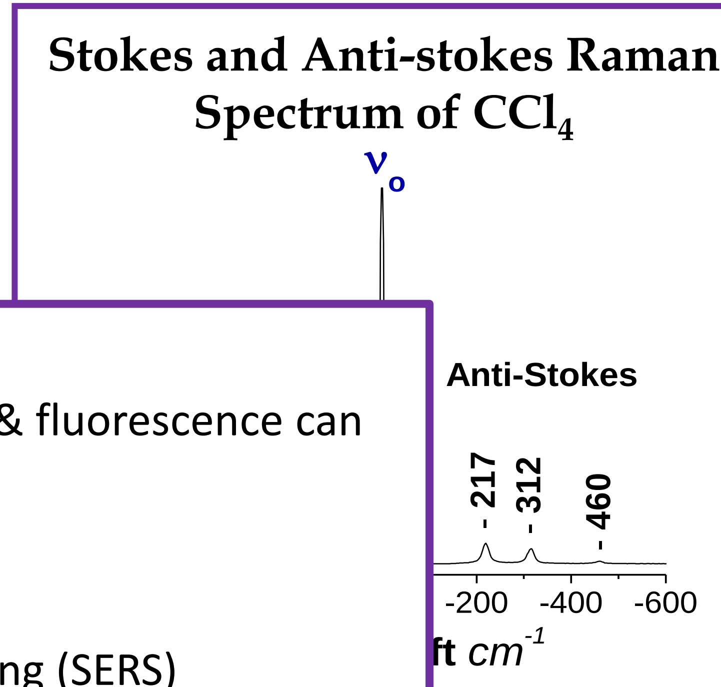


Why Raman Spectroscopy?

Raman is non-destructive and allows *in-situ* detection

Raman spectra may readily be obtained in aqueous solution (not possible with IR)



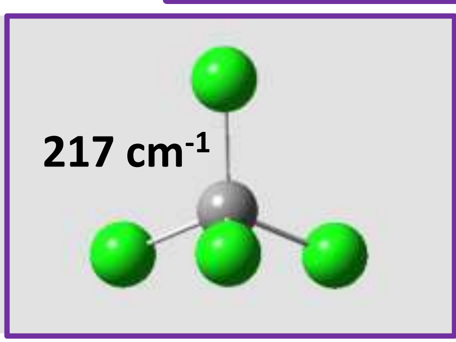


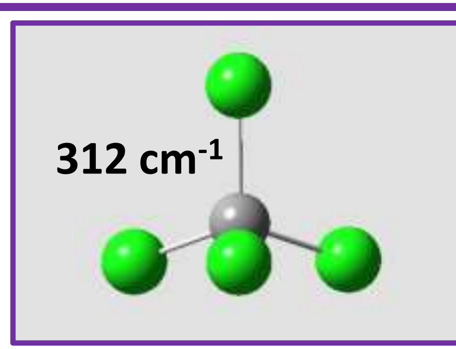
However.....

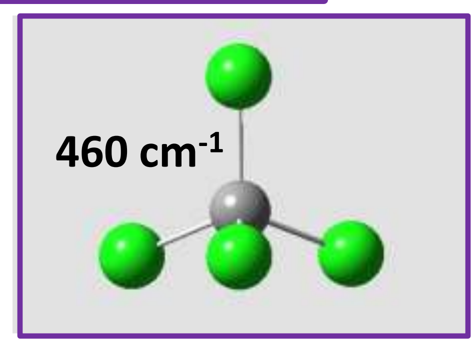
Normal Raman intensity is weak & fluorescence can contaminate spectrum

Solution!!

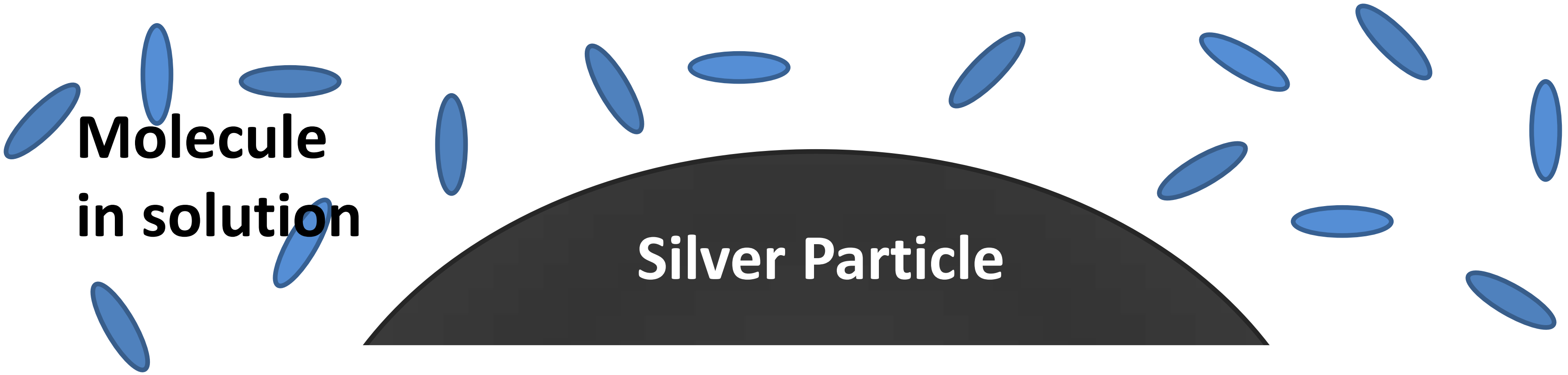
Surface Enhanced Raman Scattering (SERS)



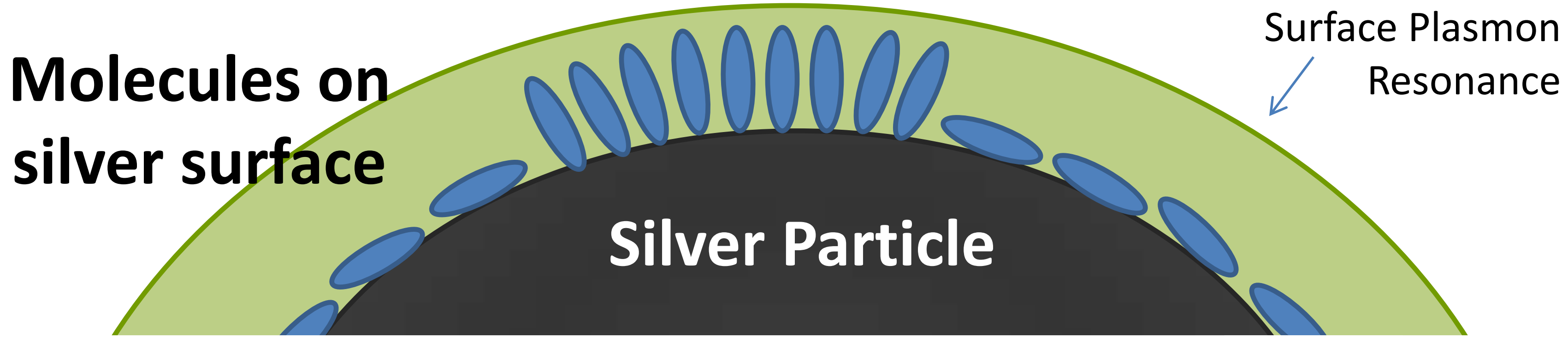




Surface Enhanced Raman Spectroscopy (SERS)



Surface Enhanced Raman Spectroscopy (SERS)

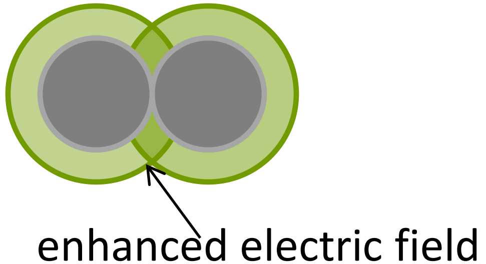


Advantages:

- **Highly sensitive**: Very large enhancements of the Raman signal. This enables us to detect and identify extremely small quantities of trace chemicals.
- **Suppresses fluorescence**: Suppression of fluorescence interference, which normally makes such identification impossible.

Factors that alter SERS intensity:

- Type of metal nanoparticle; usually silver
- Size and shape of particle
- Excitation wavelength
- Presence of ions such as Cl^-, SO_4^{2-}, NO_3^-



Surface Enhanced Raman Spectroscopy (SERS)

SERS has its own set of challenges…

- small number of compounds studied so far
- large difference in SERS efficiency even for closely related compounds
- lack of searchable databases
- interferences due to impurities or matrix components (not a separation technique)
- SERS still requires removing a sample - however microscopic - from the object under analysis

Advant

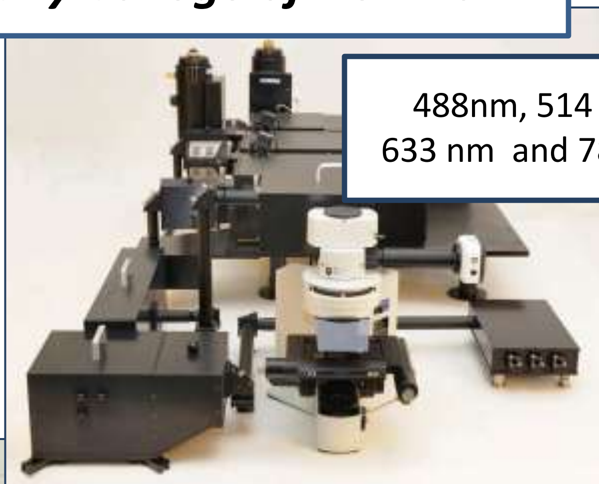
- **Highly** … gnal. This enables … of trace chemic…
- **Suppre**… rference, which r…

Factors that

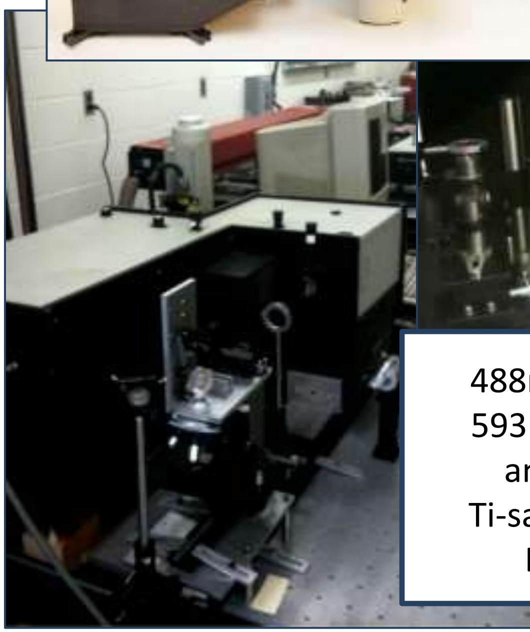
- Typ…
- Size and shape of particle
- Excitation wavelength
- Presence of ions such as Cl^-, SO_4^{2-}, NO_3^-

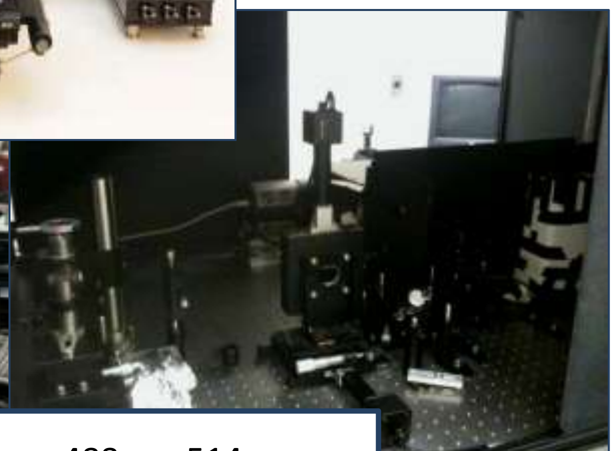
Instrumentation

City College of New York

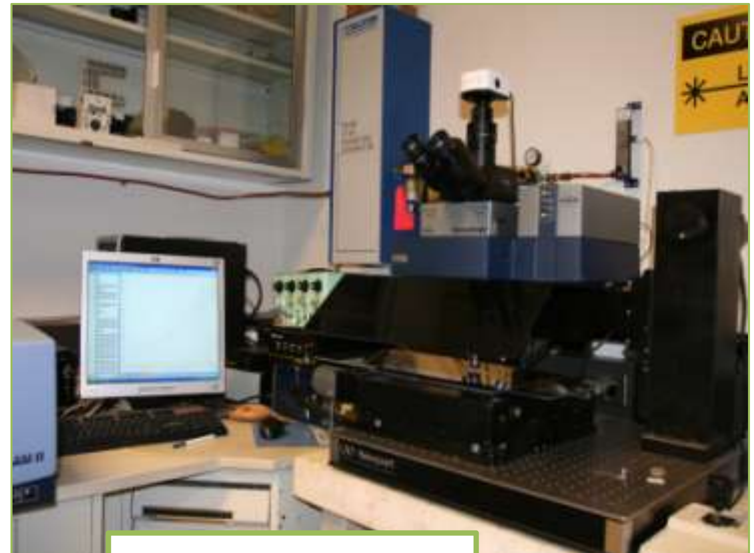


488nm, 514 nm,
633 nm and 785 nm

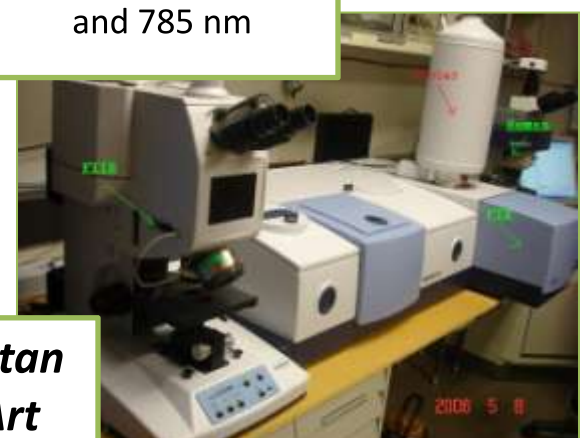




488nm, 514 nm,
593 nm, 633 nm
and 785 nm
Ti-sapphire laser
Dye laser

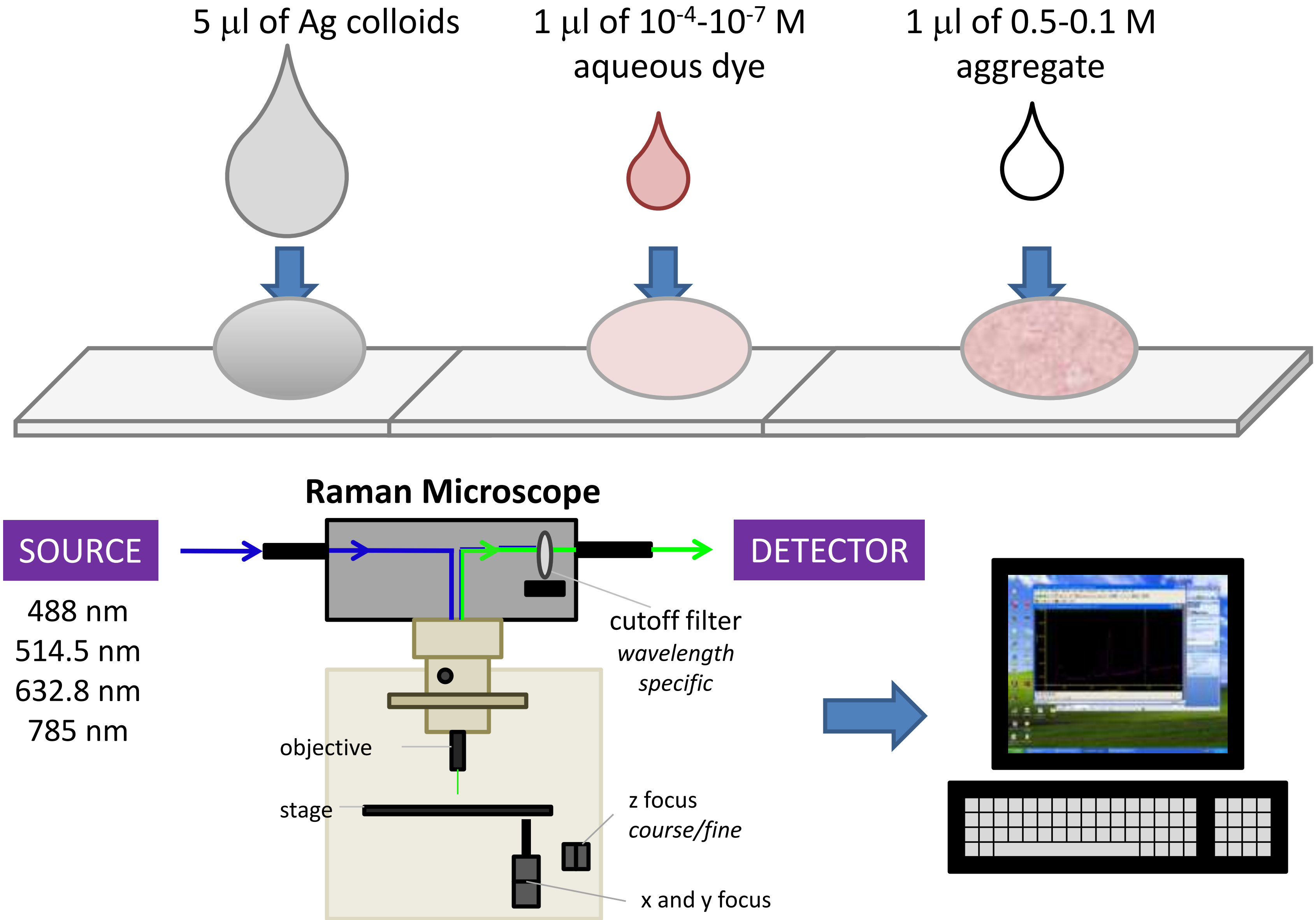


488nm, 633 nm
and 785 nm



The Metropolitan Museum of Art

Basic Steps to SERS



Current Research Projects

Developing Methods	Applications

Developing Methods

- Need ways to acquire trace amounts of analyte in a "non-destructive manner"
  Gel Extraction
- Need a reliable substrate to yield reproducible spectra
  SERS substrate

Applications

- Art History/Conservation
  Xanthene Dyes
- Forensic Science: Controlled Substances
  SERS + Amphetamine
- Forensic Science/Anthropology
  SERS of Tattoo Inks

Gel Extraction Method

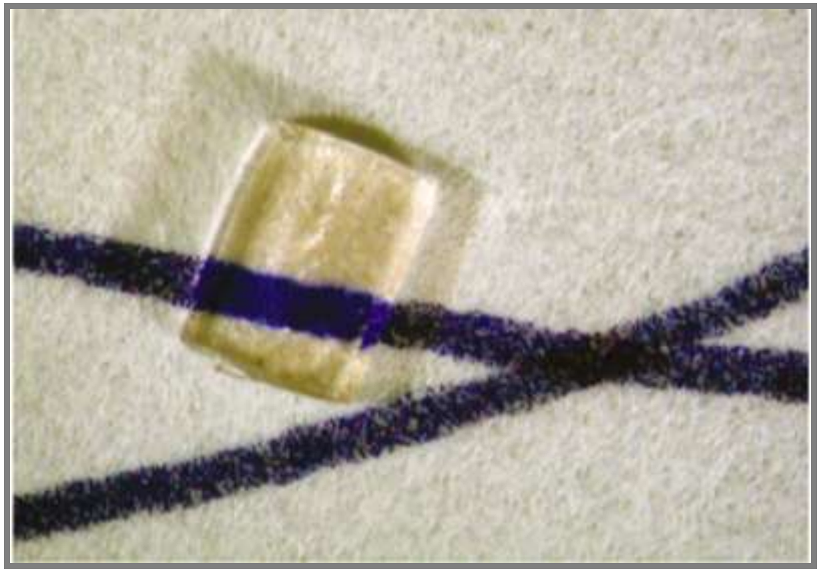
GOAL: Develop Non-Destructive Gel Extraction Method

Idea

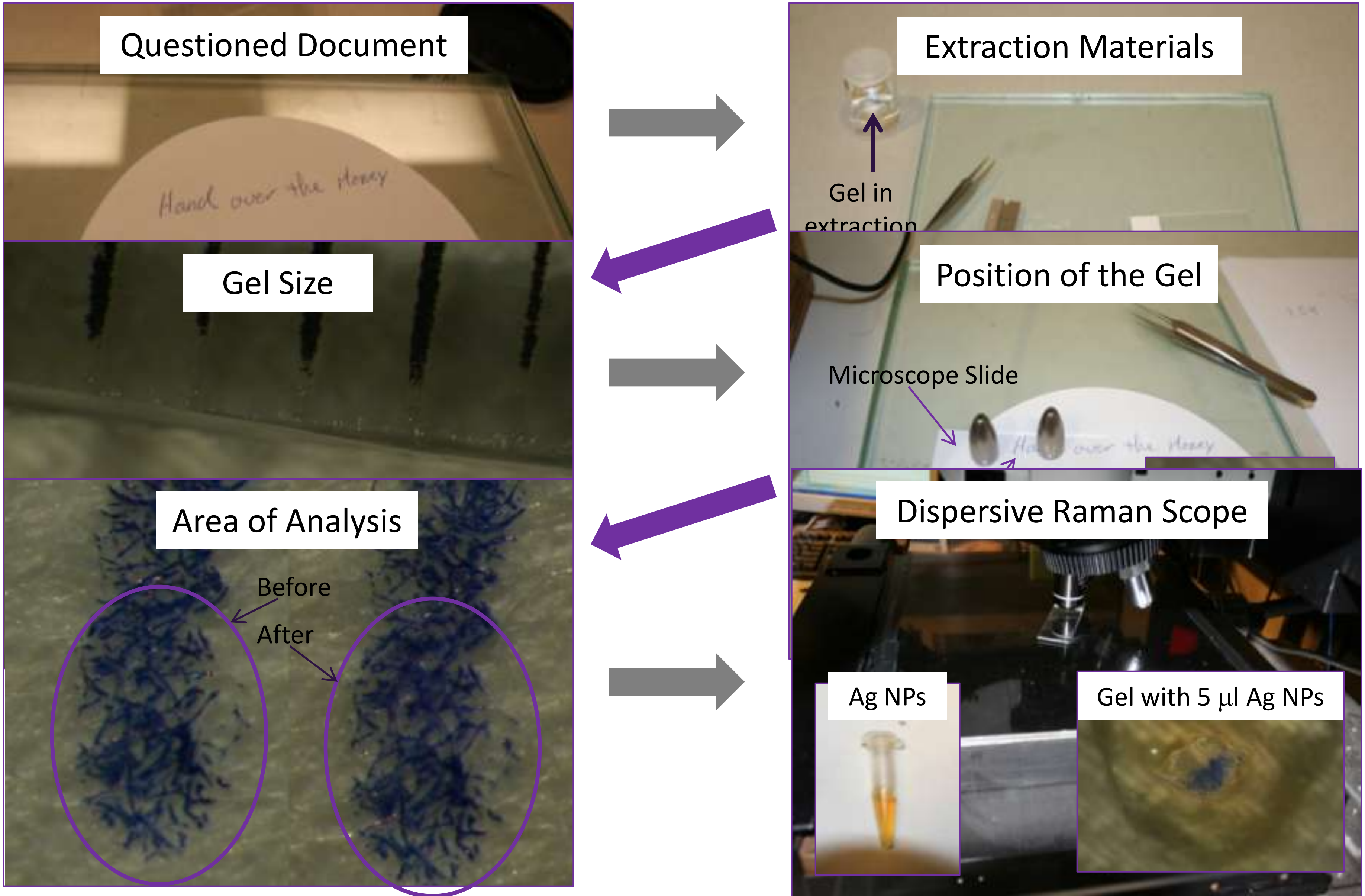
- Ink or dye can be extracted from a medium using a hydroxy gel
- The gel extracts such a small amount of dye that it leaves the test subject virtually unchanged
  - *Important in trace analysis*
- The extracted dye can then be analyzed and identified using normal Raman spectroscopy or SERS

Model System

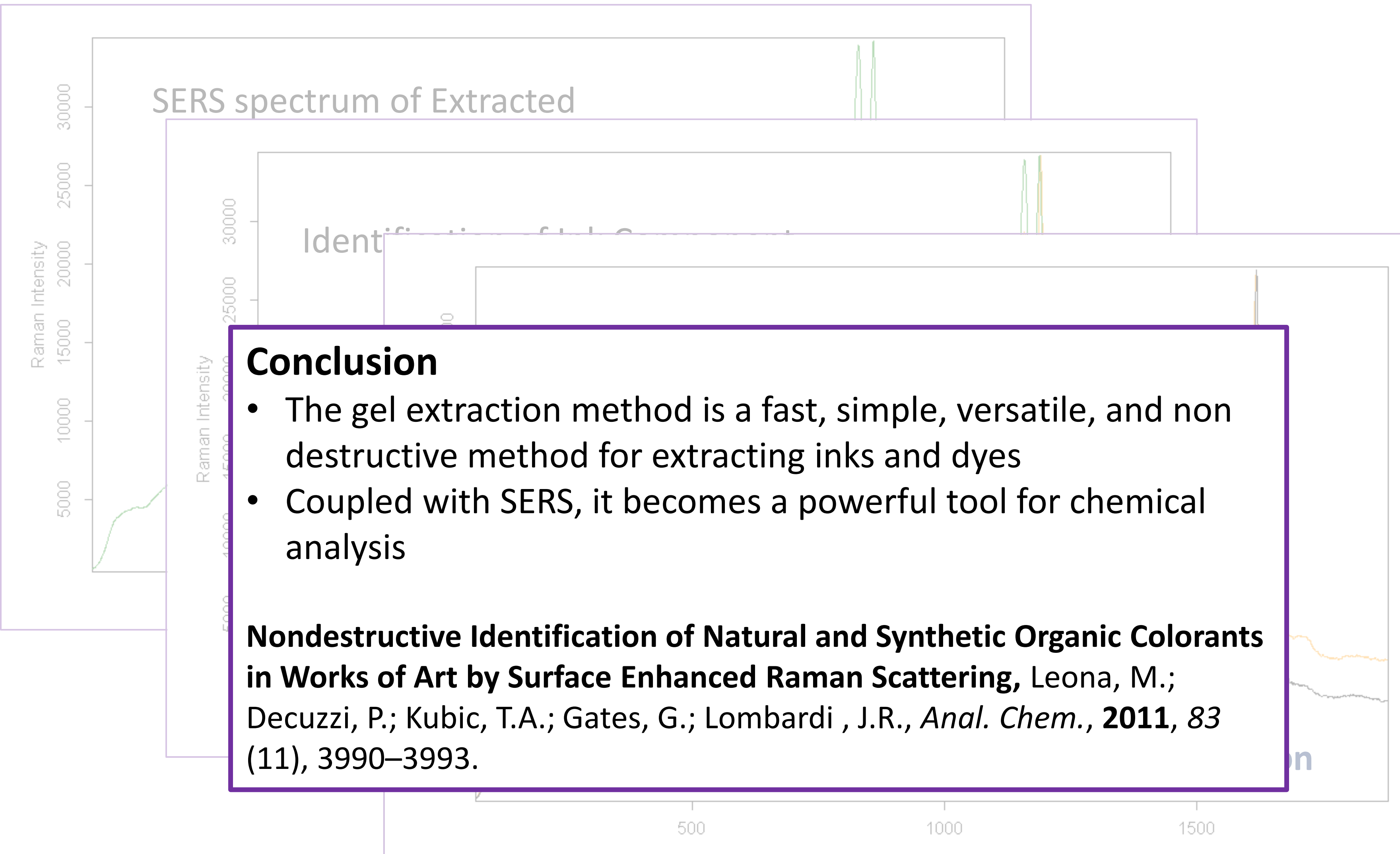
- Ball Point Pen Ink on Whatman Filter Paper



Gel Extraction Method



Gel Extraction Method



Conclusion

- The gel extraction method is a fast, simple, versatile, and non destructive method for extracting inks and dyes
- Coupled with SERS, it becomes a powerful tool for chemical analysis

Nondestructive Identification of Natural and Synthetic Organic Colorants in Works of Art by Surface Enhanced Raman Scattering, Leona, M.; Decuzzi, P.; Kubic, T.A.; Gates, G.; Lombardi , J.R., *Anal. Chem.*, **2011**, *83* (11), 3990–3993.

Refining SERS Technique

Microwave Silver NPs

GOAL: Produce and Characterize Reproducible/Stable Ag surface for SERS

Historic Method:

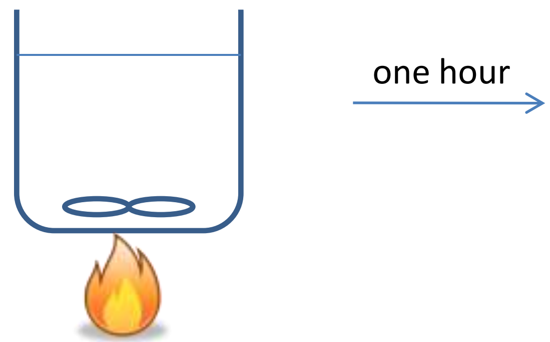
Lee-Miesel Silver NPs ($AgNO_3$ + citrate)

- broad absorption (FWHM > 120nm)
- broad size distribution (3 - 50 nm)
- not stable over time

Lee, P.C.; Meisel, D., *J. Phys. Chem.*, **1982**, *86*, 3391-3395.

$AgNO_3$ (aq) + citrate → Ag ^{0}→ Ag Nanoparticles (NP)

oxidizing agent | reducing agent



Our Method:

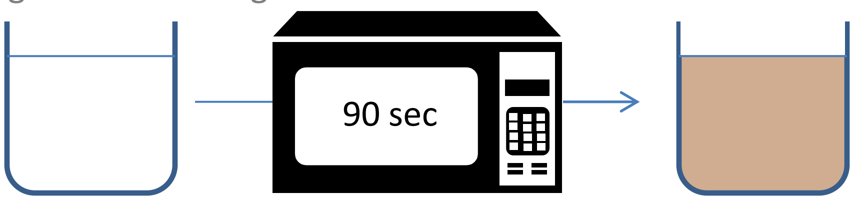
Microwave Reduction (Ag_2SO_4 + glucose + citrate)

- narrow absorption (FWHM ~ 50 nm)
- narrow size distribution (3 - 10 nm)
- stable over 5 - 12 months
- reproducible SERS spectra over time

Leona, M., *PNAS*, **2009**, 106 (35), 14757-14762

Ag_2SO_4 (aq) + sugar (+ citrate) → Ag ^{0}→ Ag NP

oxidizing agent | reducing agent



Microwave Silver NPs

Historic Method:

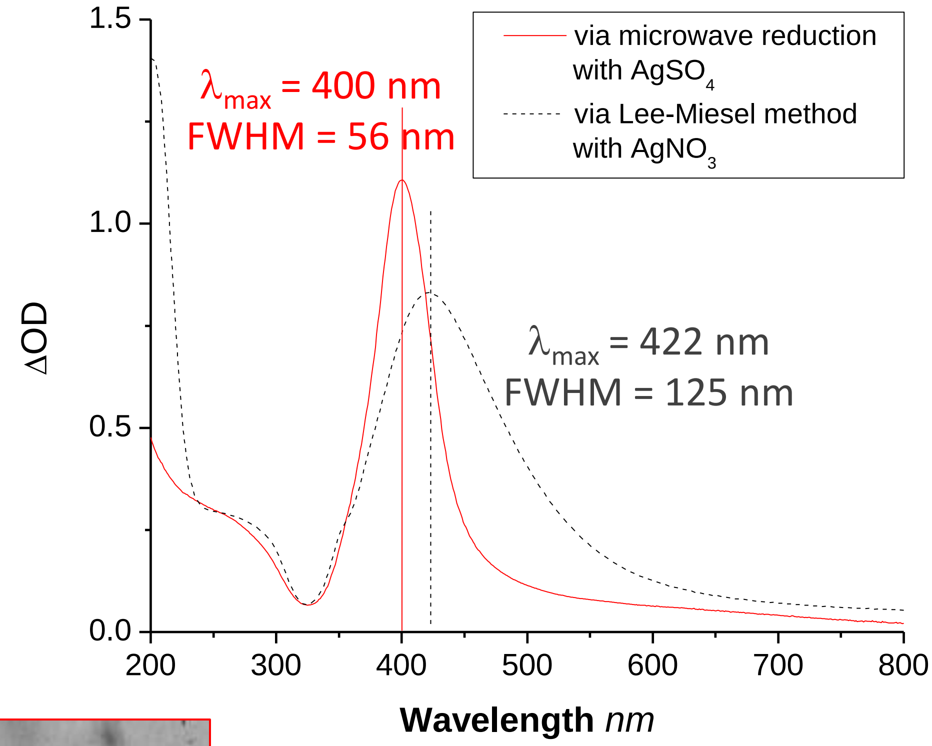
Lee-Miesel Silver NPs ($AgNO_3$ + citrate)

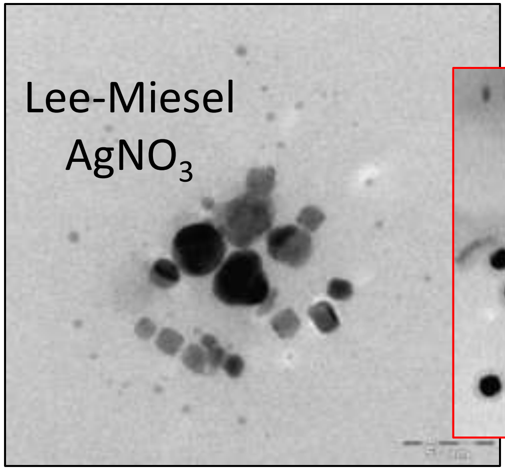
- broad absorption (FWHM > 120nm)
- broad size distribution (3 - 50 nm)
- not stable over time

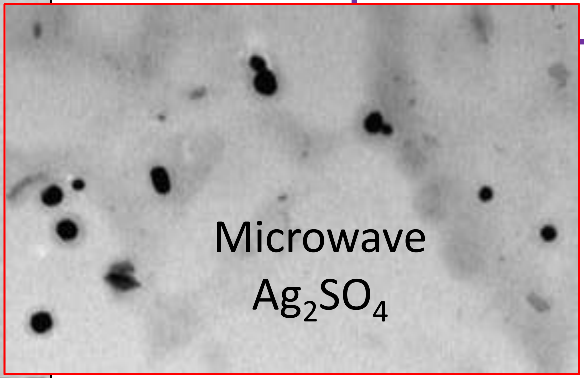
Our Method:

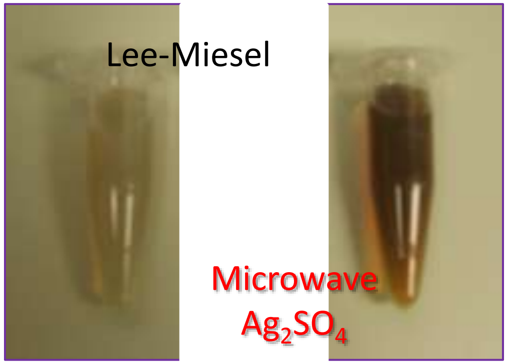
Microwave Reduction (Ag_2SO_4 + glucose)

- narrow absorption (FWHM ~ 50 nm)
- narrow size distribution (3 - 10 nm)
- stable over 5 - 12 months
- reproducible SERS spectra over time

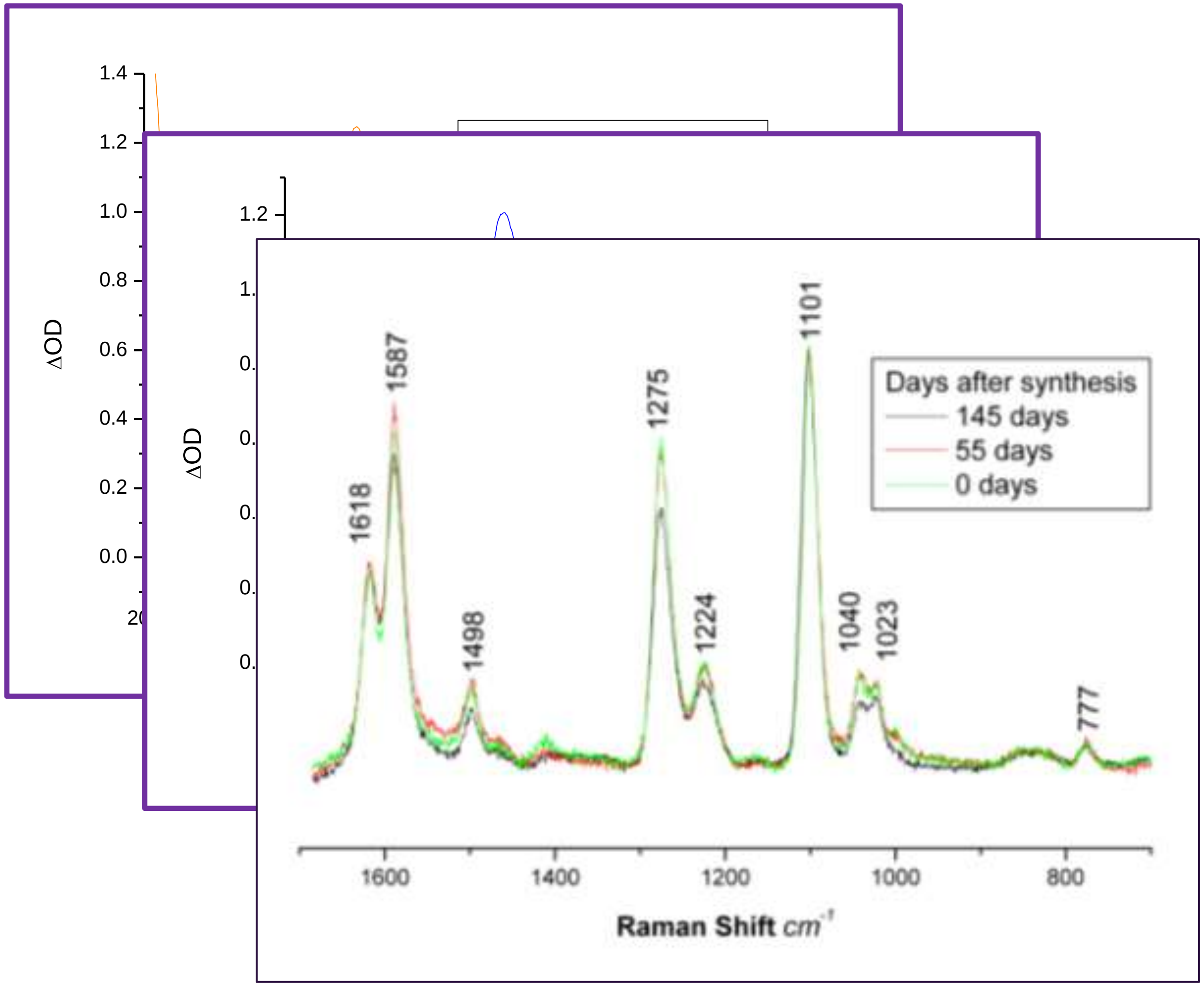


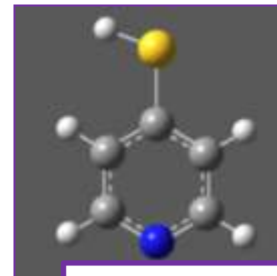






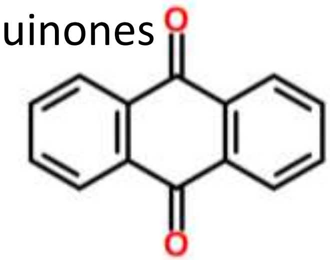
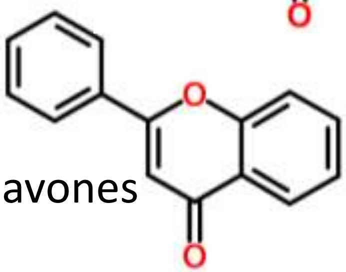
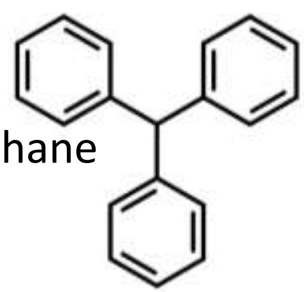
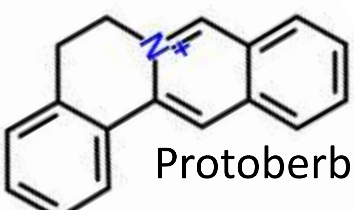
Microwave Silver





SERS Model System:
4-mercaptopyridine

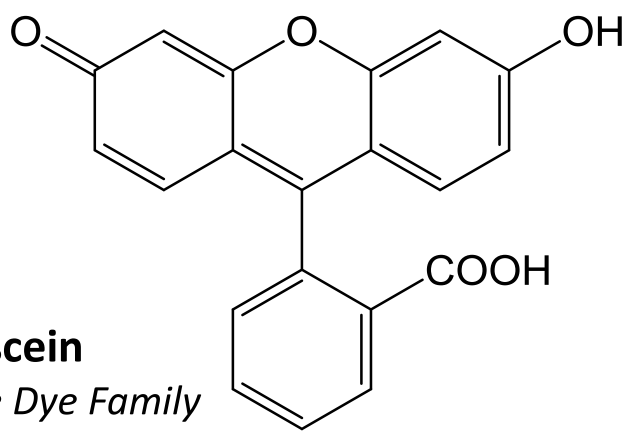
SERS of Various Dyes Classes

Dye Class	Publication
Anthraquinones 	**Surface-enhanced Raman Spectroscopy study of the red dye laccaic acid** Cañamares, M.V., et al., *J. Raman Spectrosc.*, **2007**, *38*, 1259-1266. ***Surface Enhanced Raman Spectroscopy of Indanthrone and Flavanthrone*** Chang, J.; et al., *J. Raman Spectrosc*., **2009**, *40*, 1557-1563.
Flavones 	***Raman and Surface Enhanced Raman Spectra of Flavone and Several Hydroxy-Derivatives*** Teslova, T.; et al., *J. Raman Spectroscopy*, **2007**, *38*, 802-818. ***Raman and Surface Enhanced Raman Spectra of Chrysin, Apigenin and Luteolin*** Corredor, C.; et al., V*ibrational Spectroscopy*, **2009**, *49*, 190-195. ***Raman and Surface Enhanced Raman Spectra of 7 and 3',4' Hydroxyflavone*** Cañamares, M.V.; et al., *Journal of ePreservationScience* (Proceedings of the IRUG-8, Vienna Austria, Conference), **2009**, *6*, 81-88.
Arylmethane 	***DFT, SERS, and Single Molecule-SERS of Crystal Violet*** Cañamares, M.V.; et al., *J. Phys. Chem. C*, **2008**, *112*, 20295-20300. ***Application of Raman spectroscopy and surface-enhanced Raman scattering to the analysis of synthetic dyes found in ballpoint pen ink*** Geiman, I.; et al., *J. Forensic Sci.*, **2009**, *54*, 947-952.
 Protoberberines	**Surface-enhanced Raman scattering of protoberberine alkaloids** Cañamares, M.V.; et al., *J. Raman Spectrosc.*, **2008**, *39*, 1907-1914.

Art History Application

GOAL: Characterize SERS spectrum of Halogenated Xanthene Dyes

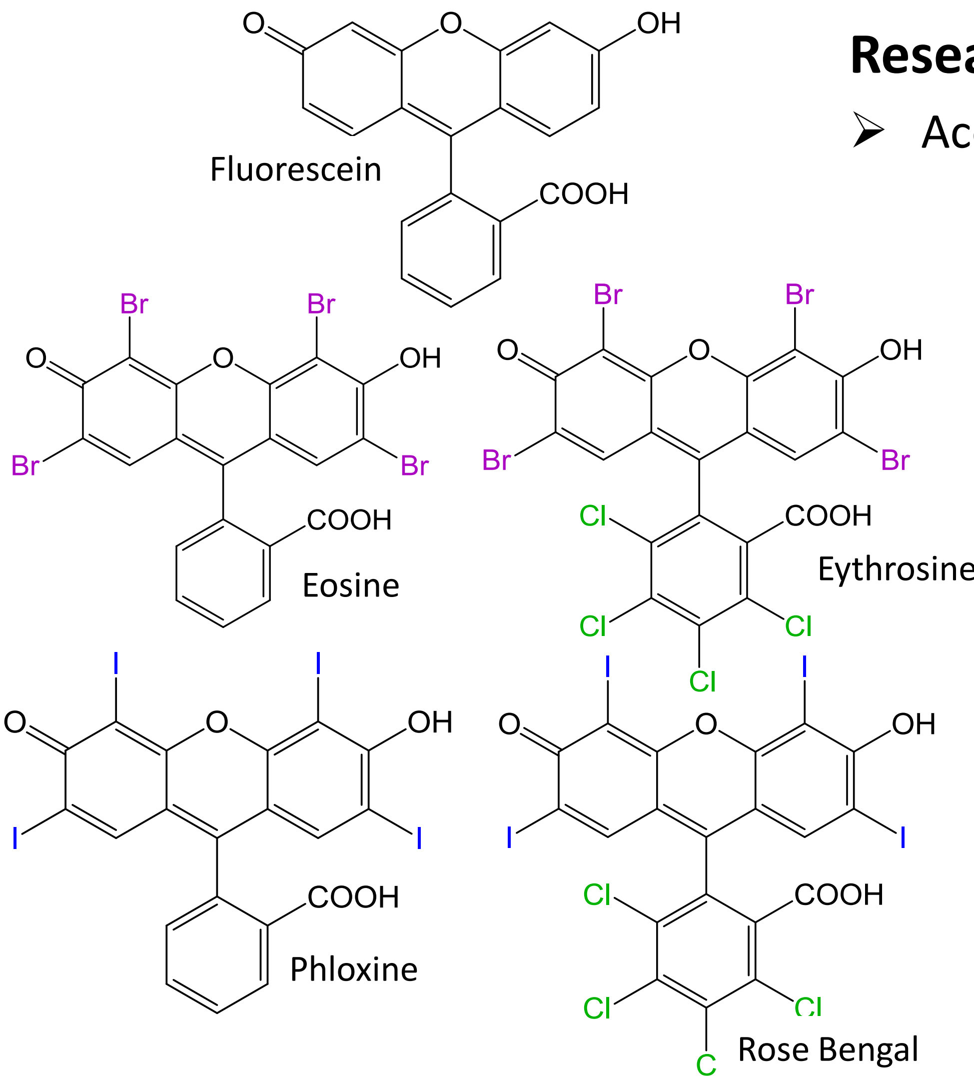
- Want to Identify Dyes in Art
  - Art Conservation
  - Art History
  - Archeology
- large number of dye classes
  - we have investigated 10 dyes classes (75 dyes total)
- Van Gogh was known to use Xanthene Dyes



Flourescein

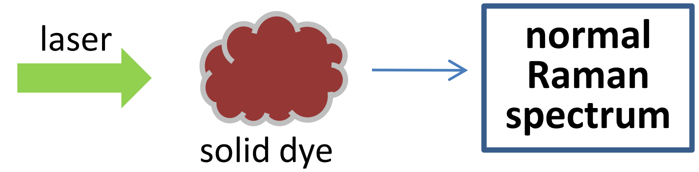
From Xanthene Dye Family

Xanthene Dyes: *A Spectroscopic Study*

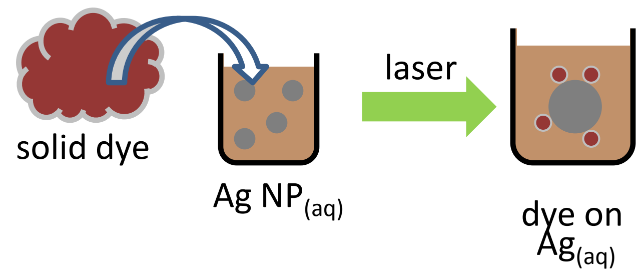


Research Strategy:

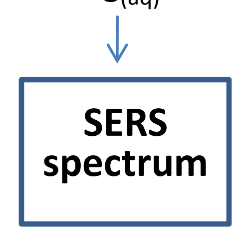
- ➢ Acquire normal Raman spectrum of each dye



- ➢ Acquire SERS spectrum of each dye

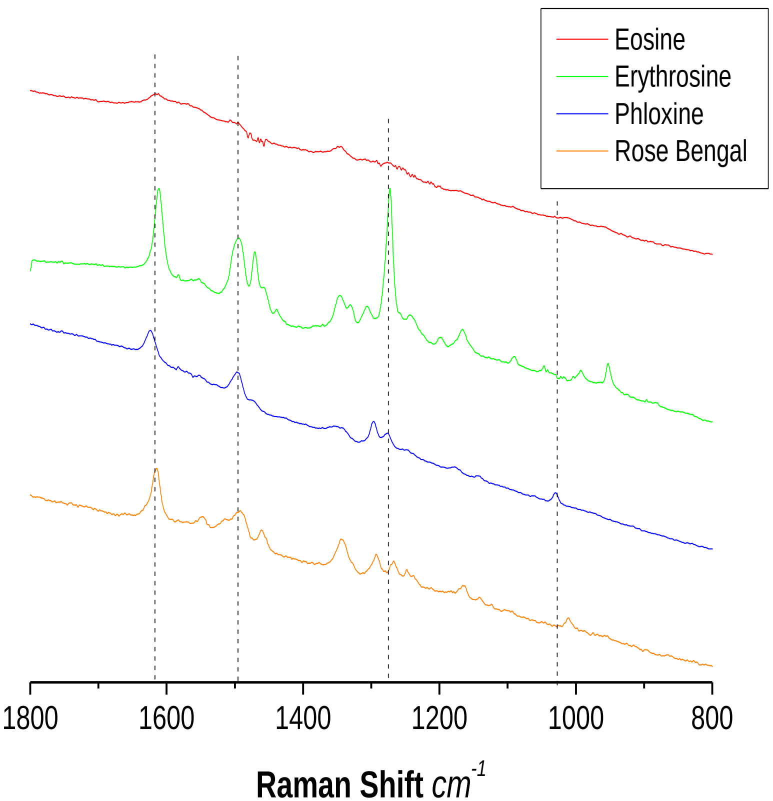


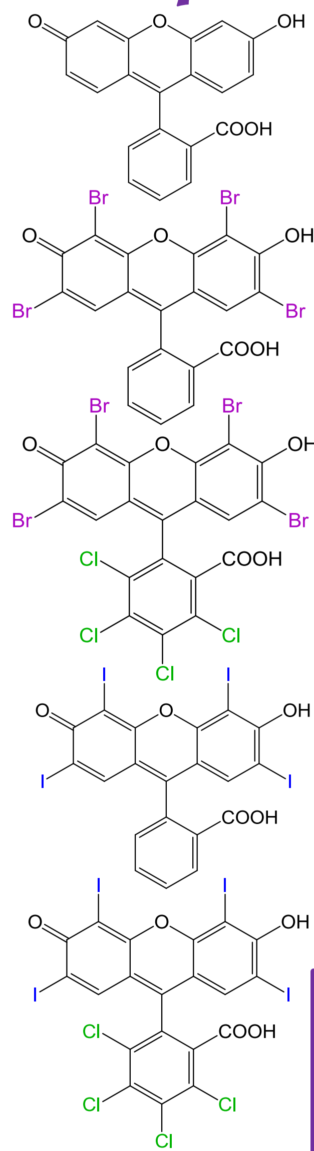
- ➢ Assign Raman Bands to Vibrational Modes
- ➢ Generate SERS Library



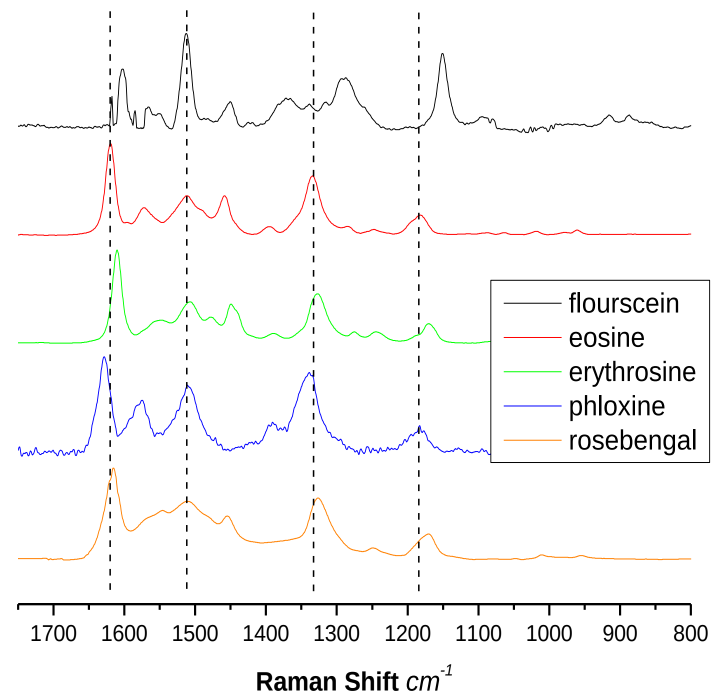
Xanthene Dyes: *A Spectroscopic Study*

Normal Raman spectra





SERS spectra



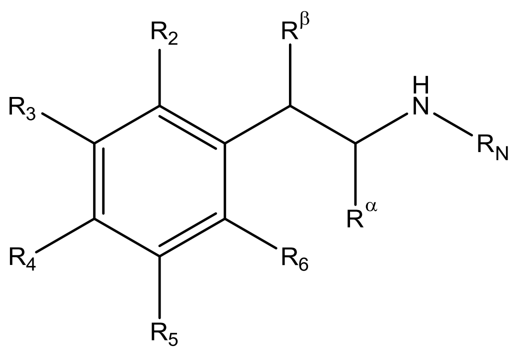
- Spectra varies upon Halogenation
- Should be able to differentiate in mixtures

Surface-Enhanced Raman Scattering of Phenethylamines

Previous SERS work on Controlled Substances:
"Surface-Enhanced Raman Spectroscopy for Trace Identification of Controlled Substances: Morphine, Codeine, and Hydrocodone"
Rana, V.; Cañamares, M.V.; Kubic, T.; Leona, M.; Lombardi, J.R.; *Journal of Forensic Sciences,* **2010**, *55*(1), 200-207.

Ecstacy

Over 175 different Phenethylamines



Phenethylamine

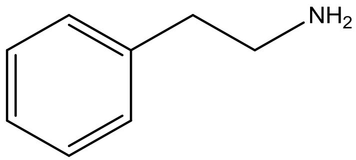
The METH makeover

wide variety of therapeutic classes, including but not limited to..

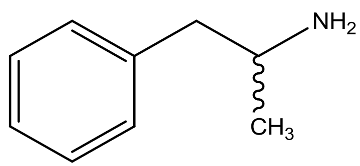
- appetite depressants
- vascoconstrictors
- psychotropic drugs
- bronchodilators
- antidepressants
- Antiparkinson agents
- neurotransmitters

SERS of Phenethylamines

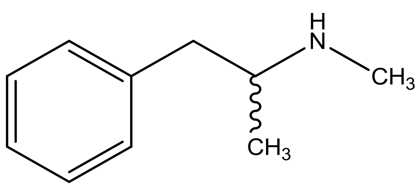
GOAL: Acquire SERS of Amphetamines for trace analysis



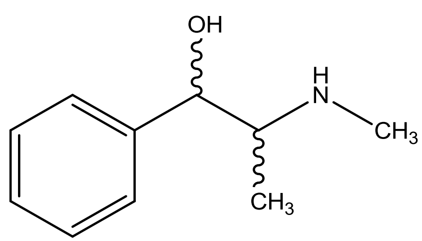
Phenethylamine



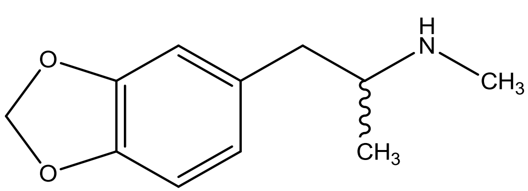
Amphetamine



Methamphetamine



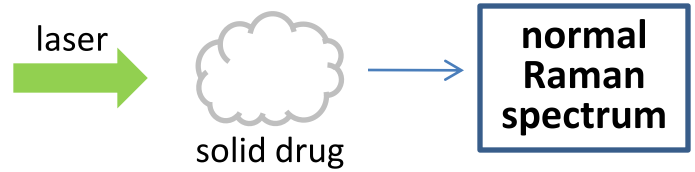
Ephedrine



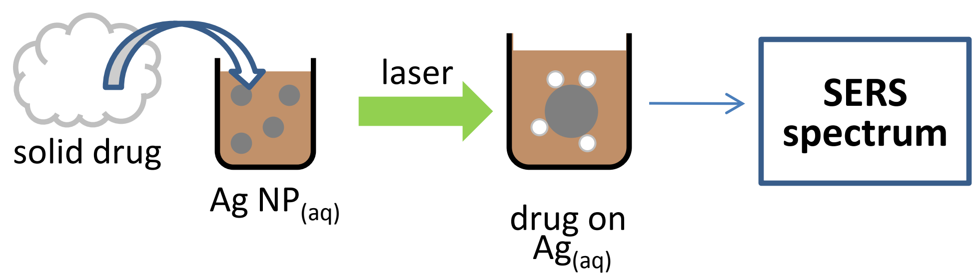
MDMA *(Ecstasy)*

Research Strategy:

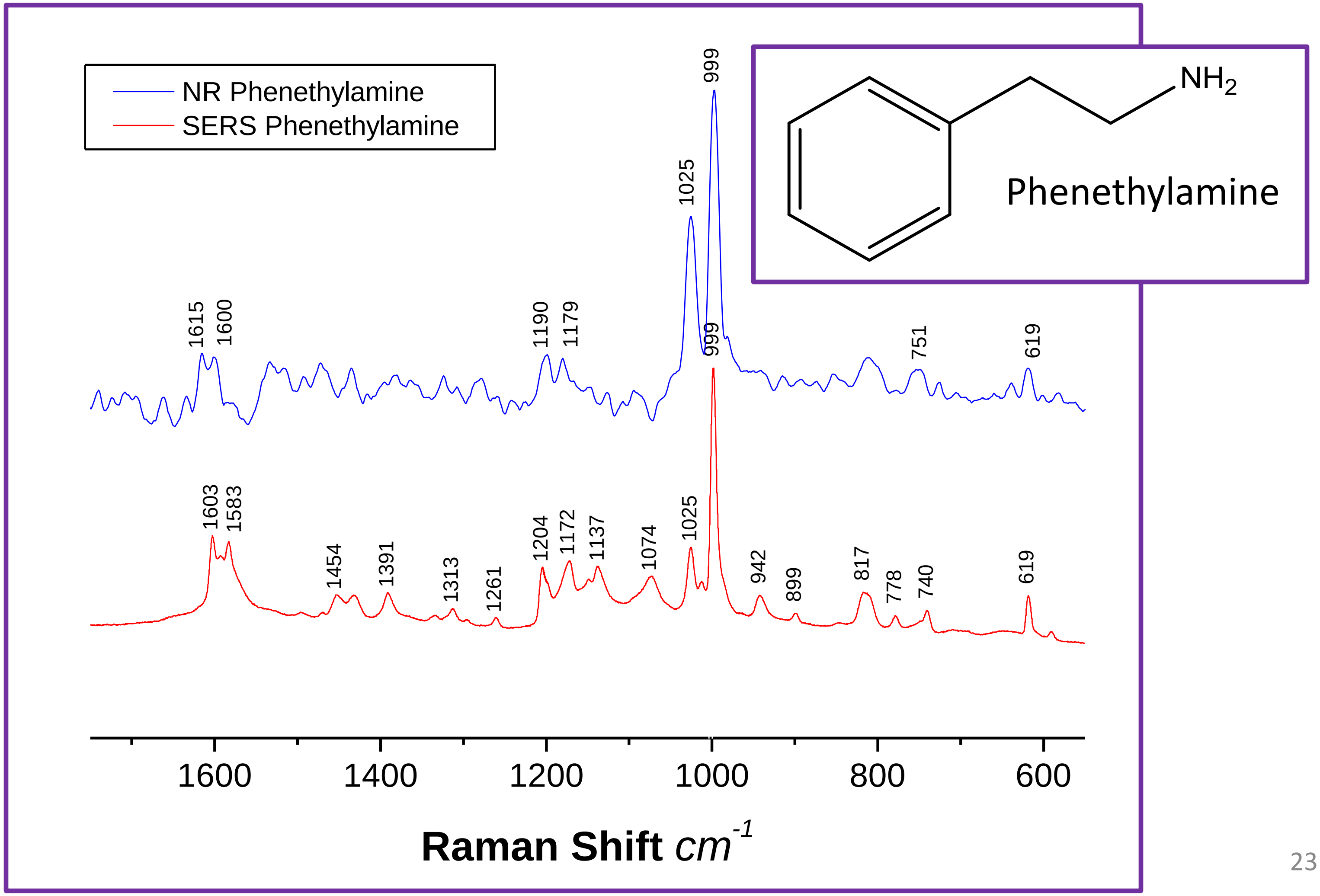
- Acquire normal Raman spectrum of Phenethylamines



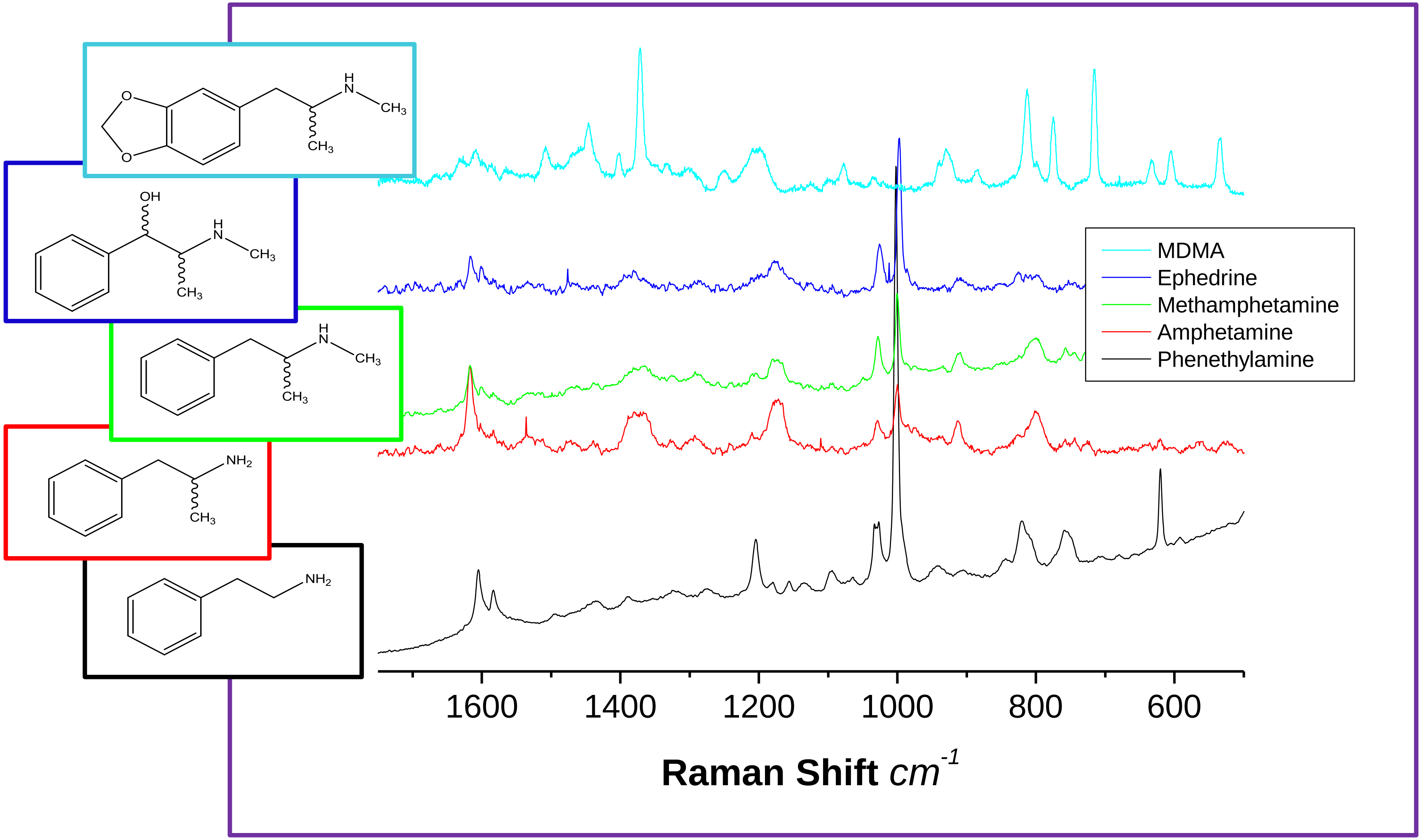
- Acquire SERS spectrum of Phenethylamines, refining experimental conditions



Normal Raman and SERS of Phenethylamine



SERS of Phenethylamine

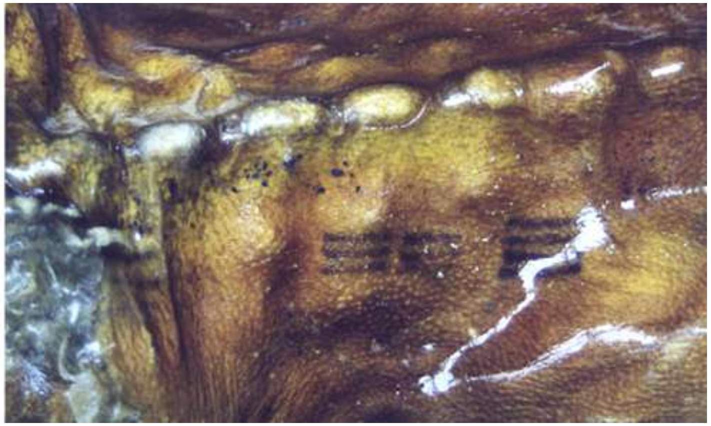


Surface-Enhanced Raman Scattering of MDMA (Ecstasy) and Analogs

Taplin, F.; O'Donnell, D.; Kubic, T.; Leona, M.; Lombardi, J.R., *Forensic Science International* - submitted

Raman Scattering of Tattoo Inks

Anthropological Implications



Pulled from the Headlines….

Man Arrested for Tattooing Toddler

Parents Arrested for Home-Tattooing 6 Children

KTLA News
11:24 AM PST, January 4, 2010

Dad Charged With Tattooing 3-Year-Old Son

Man tattoos gang symbol on 7 y.o. son

Police Dept. will pay to have tattoo removed

Worst tattoo ever? Amateur pranks friend by giving him obscene ink instead of yin-yang he asked for
NY DAILY NEWS
Tuesday, October 26th 2010, 4:28 PM

Raman Scattering of Tattoo Inks

GOAL: Acquire SERS of Tattoo Inks

- Most work on Tattoo inks in the past have used Absorption Spectroscopy, IR, XRD and SEM.
- Some work has been done using Dispersive Raman looking at carbonous materials in tattoos*

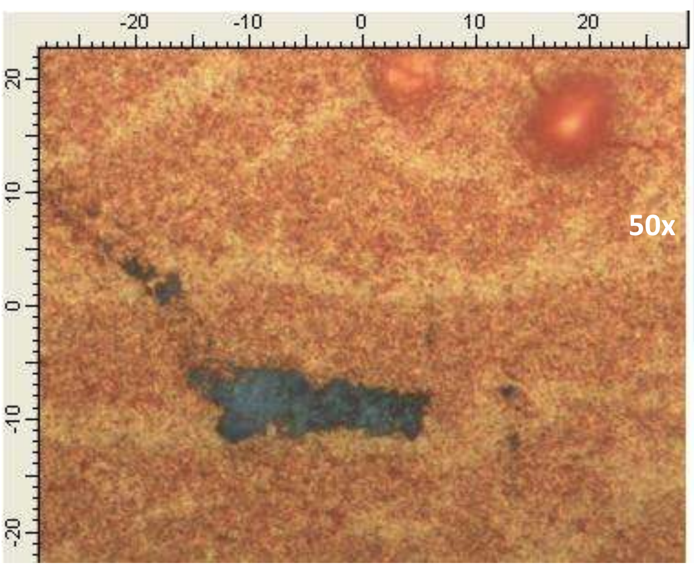
Iron Works Brasil (10)- Brazil

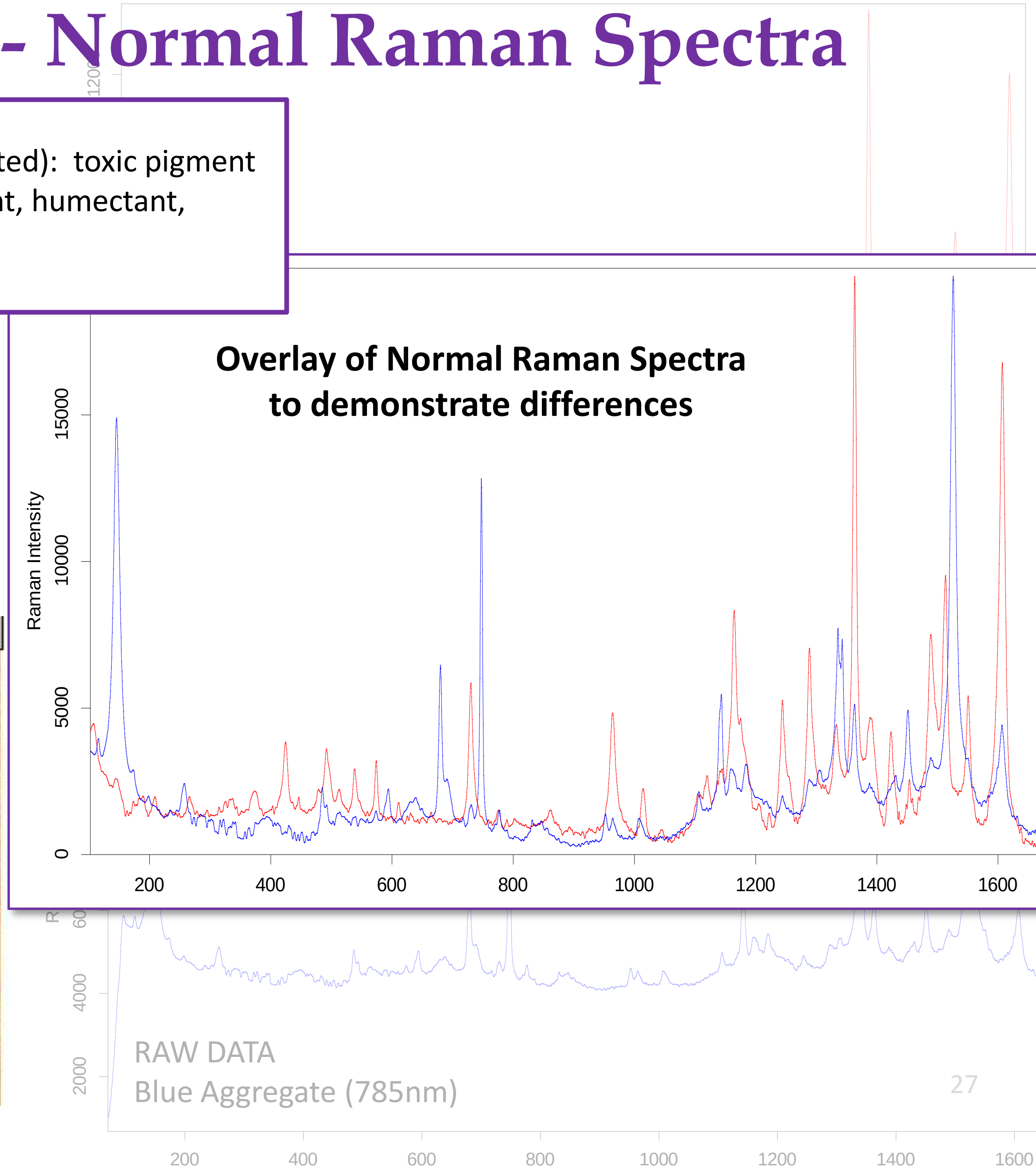
Skin Candy (17)- USA

* Poon, K.; I. Dadour, I.; McKinley, A., *J. of Raman Spectroscopy*, **2008**, *39*, 1227-1237.
Poon, K.W.C., M.S./Ph.D. Thesis, The University of Western Australia, 2008.

Tattoo Inks - Normal Raman Spectra

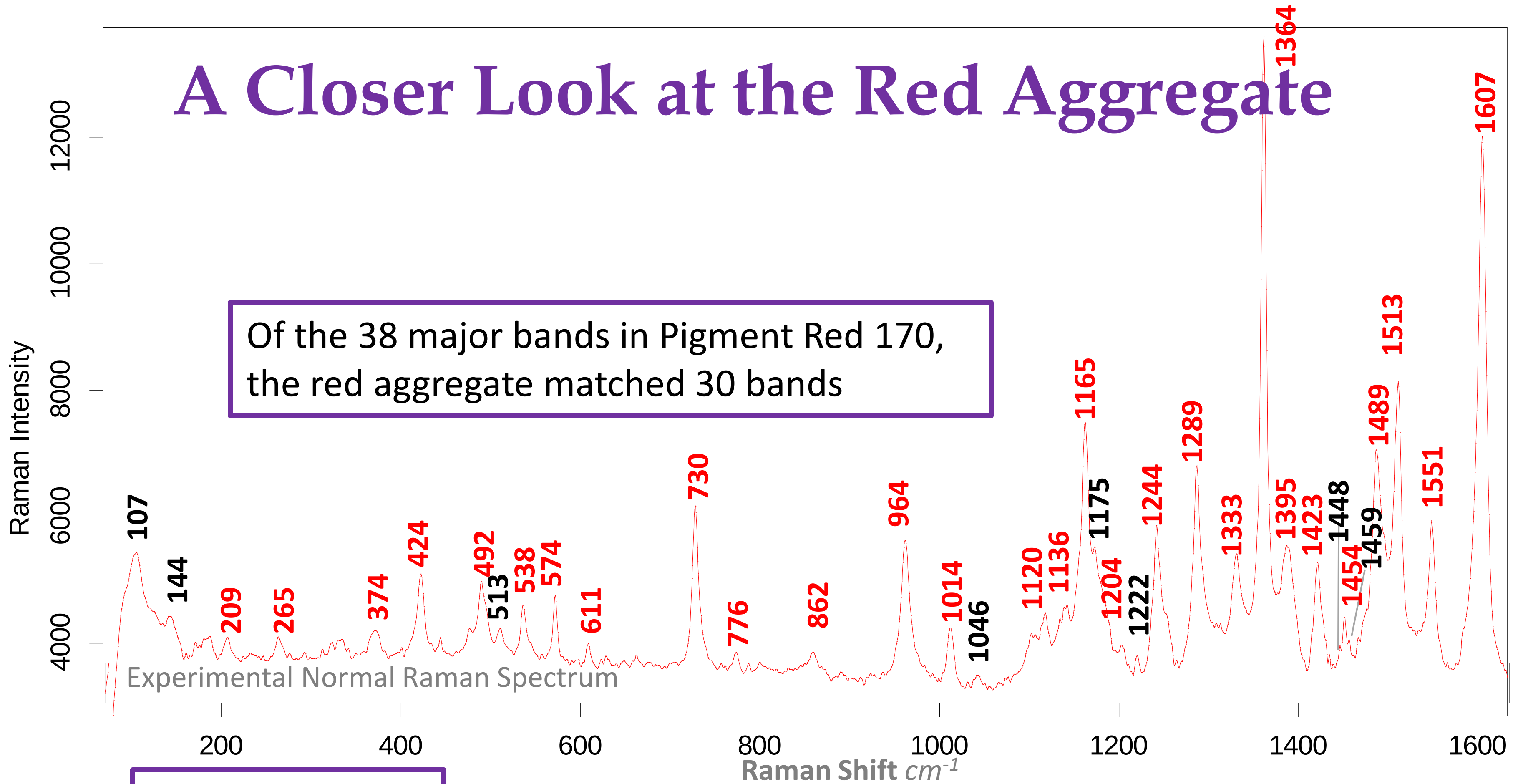
Vermelho-Iron Works Brasil
Ingredients (according to packaging; translated): toxic pigment (mineral/organic) deionized water, surfactant, humectant, preservative
NOTE: No color information provided

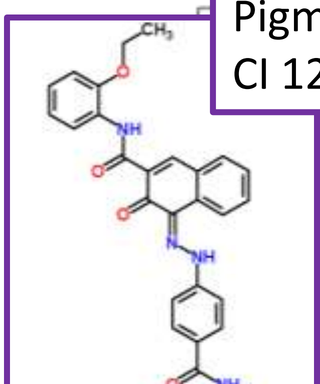




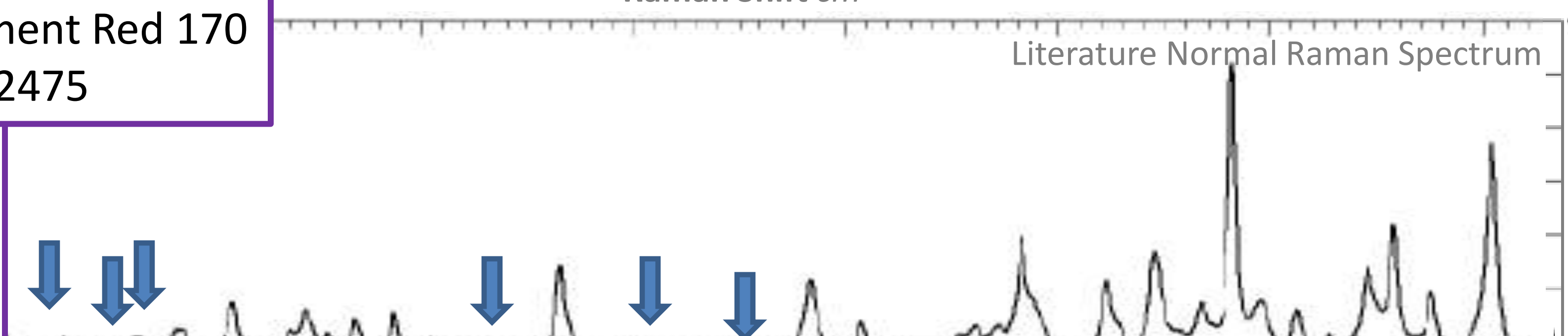
A Closer Look at the Red Aggregate

Of the 38 major bands in Pigment Red 170, the red aggregate matched 30 bands



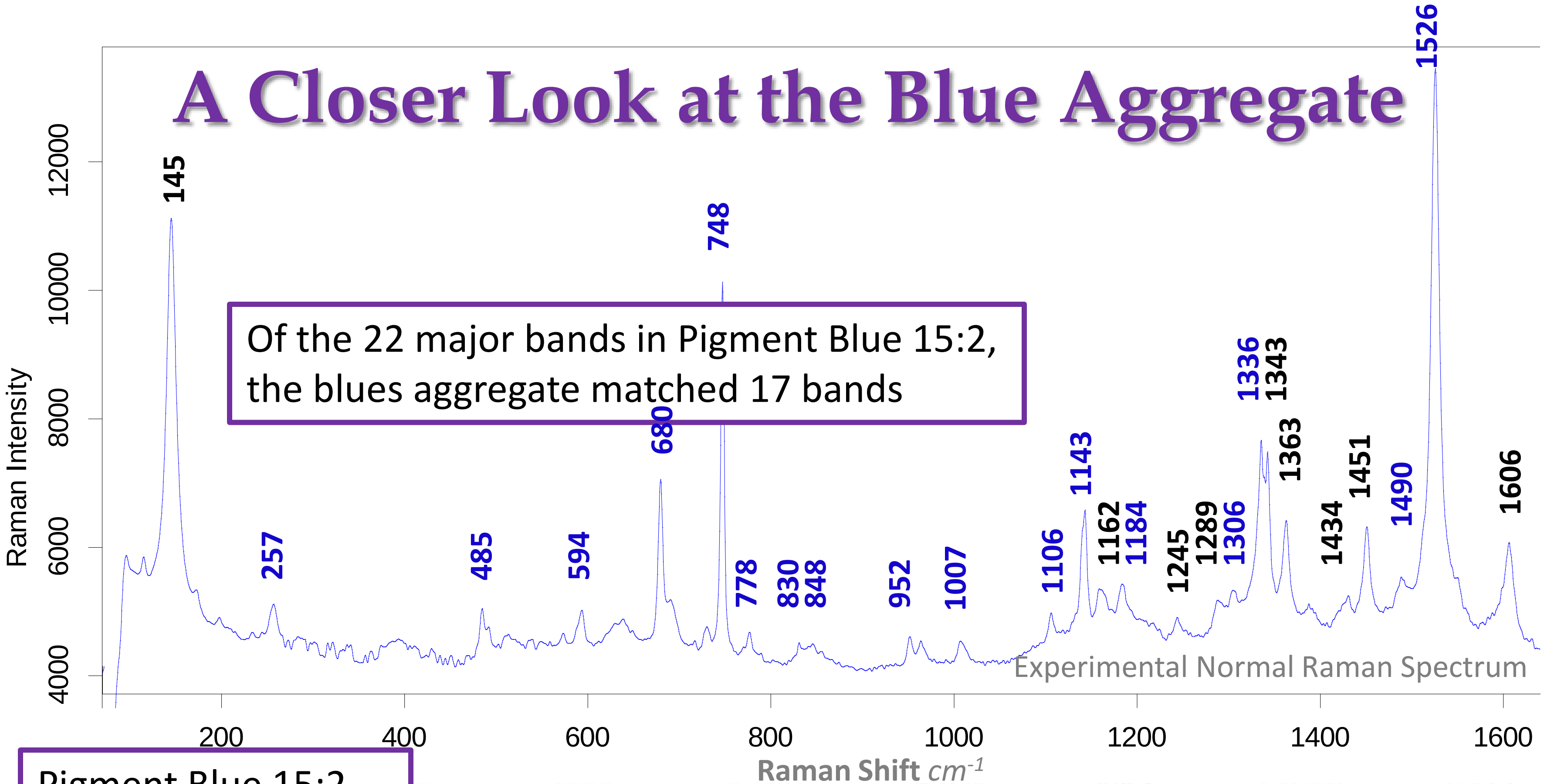


Pigment Red 170
CI 12475



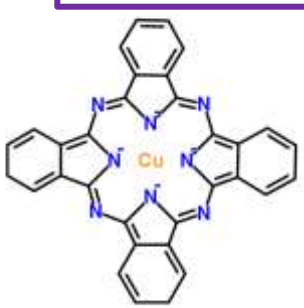
Scherrer, N., Z., et al., *Spectrochimica Acta Part A*, 2009, Vol. 73, 505-524.

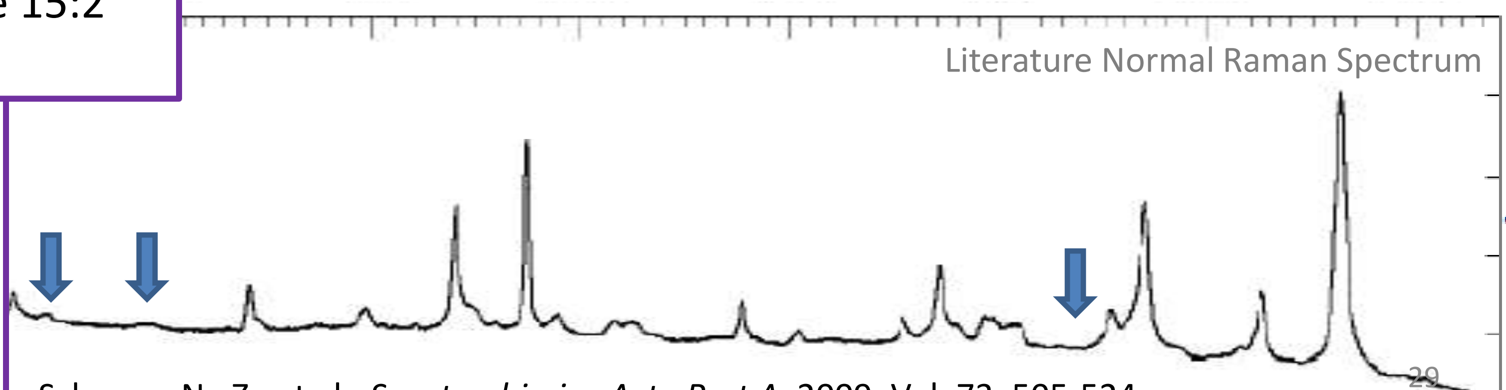
A Closer Look at the Blue Aggregate



Of the 22 major bands in Pigment Blue 15:2, the blues aggregate matched 17 bands

Pigment Blue 15:2
C.I 74160



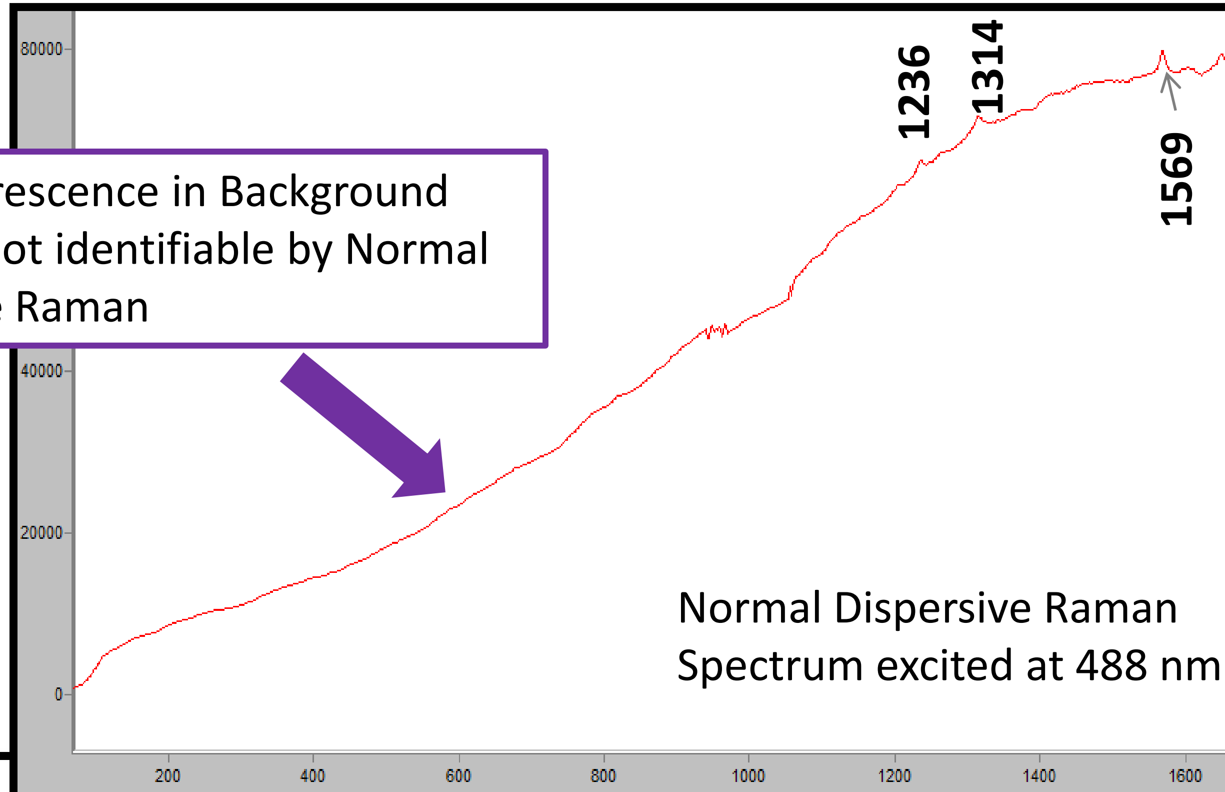


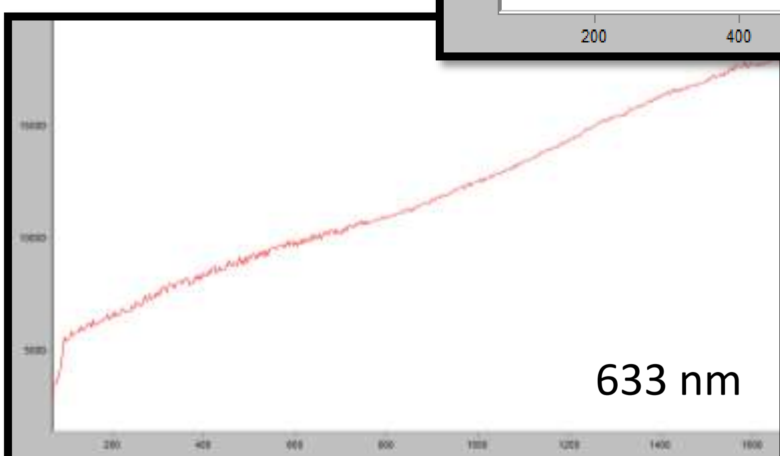
Scherrer, N., Z., et al., *Spectrochimica Acta Part A*, 2009, Vol. 73, 505-524.

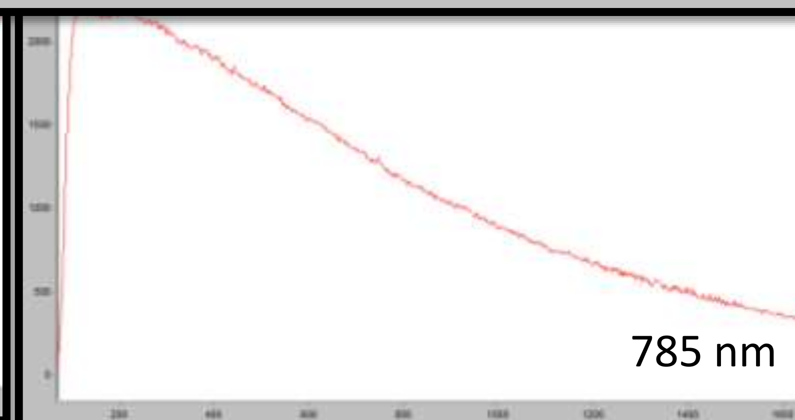
SERS of Tattoo Inks

Razberry Creem
Skin Candy
Pigment Red 122

- High Fluorescence in Background
- Pigment not identifiable by Normal Dispersive Raman

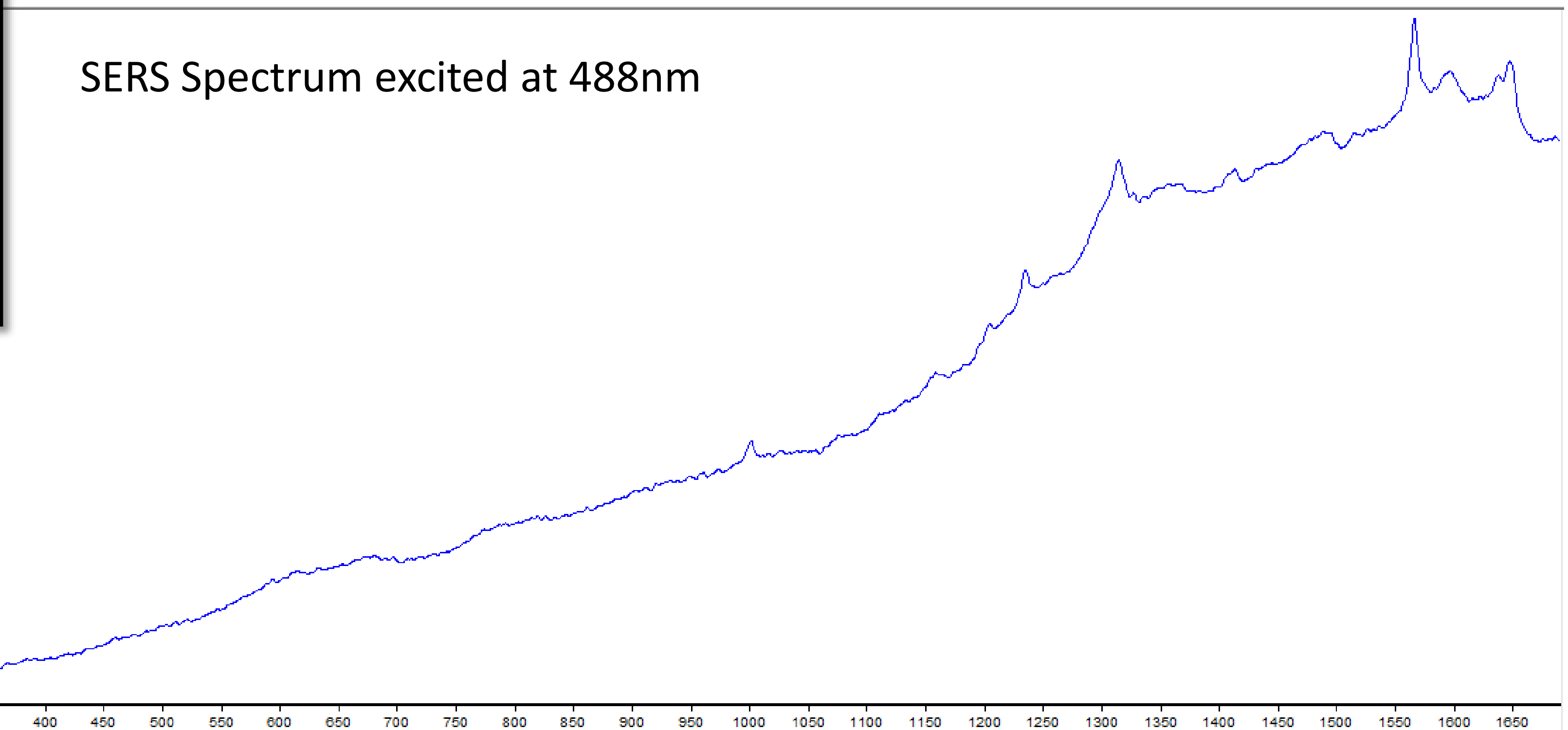






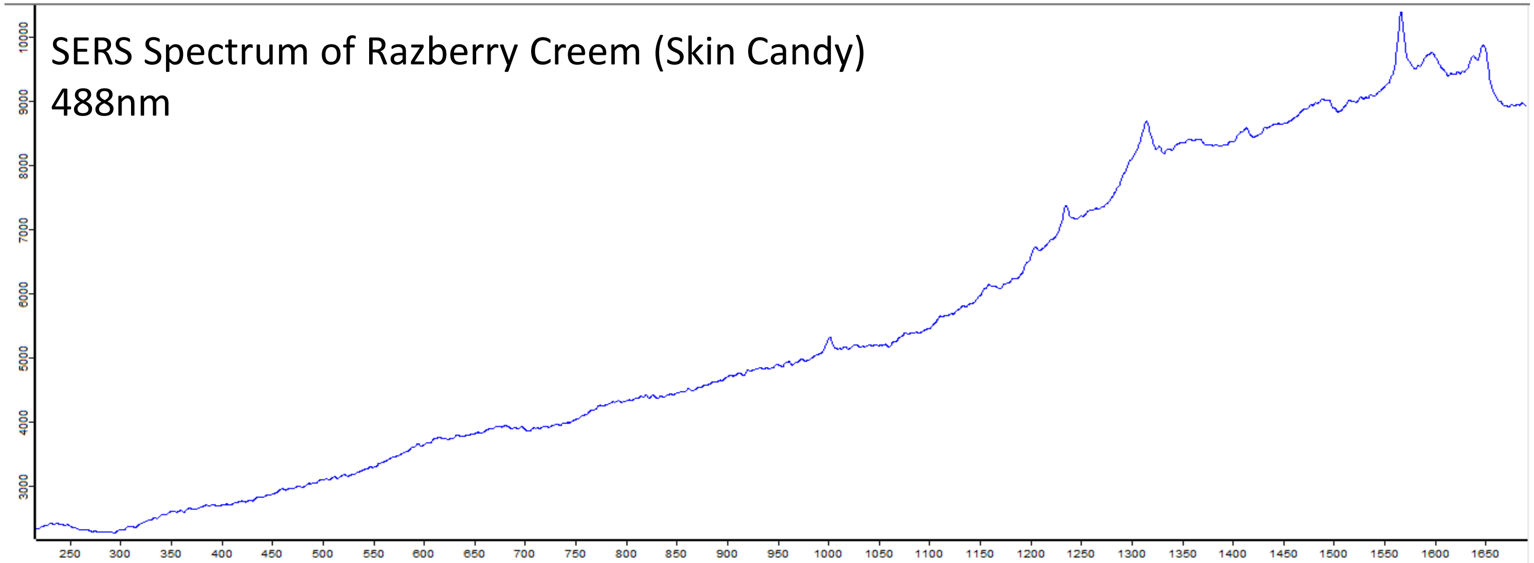
Razberry Creem
Skin Candy
Pigment Red 122

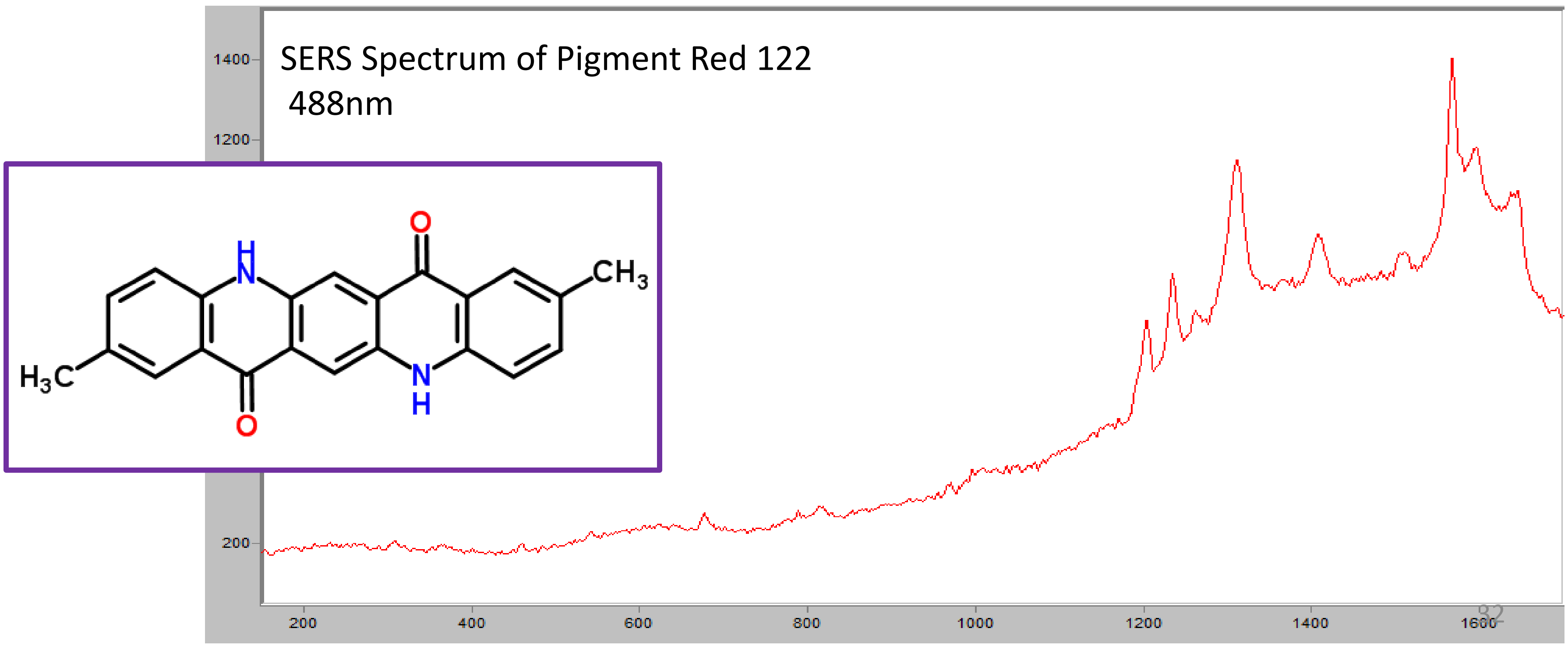
SERS Spectrum excited at 488nm



Note: Enhancement of three weak bands (1568, 1316 and 1238 cm^{-1}) and additional peaks resolved


Skin Candy
azberry Creem


SERS Spectrum of Razberry Creem (Skin Candy)
488nm


SERS Spectrum of Pigment Red 122
488nm
1400
1200
200
200
400
600
800
1000
1200
1400
1600
H
N
O
CH3
H3C
O
N
H

Research Summary

Developing Methods

Gel Extraction

- Successfully extract and identify trace amounts
- Methodology is system specific

SERS substrate

- Ag NP synthesis by microwave reduction yields reliable, reproducible surface
- Stable for at least 5 months

Applications

Xanthene Dyes

- Developing SERS Library
- Future Work: Mixtures

SERS + Phenethylamine

- 5 Phenethylamines characterized

SERS of Tattoo Inks

- Tattoo Inks are heterogeneous, present challenge
- Work is ongoing

Other Areas of Research

TLC + SERS

- SERS can improve detection limit beyond visible detection
- Separation and Identification of complex mixtures

SERS of Dye/Drug mixtures

- Engineered Mixtures and Real Samples

Acknowledgments

Prof. John Lombardi – *research advisor (CCNY)*
Dr. Marco Leona – *research advisor (Metropolitan Museum of Art)*
Patrick Buzzini - *collaborator (West Virginia University)*
Phillip Antoci - *collaborator (NYPD Crime Labs)*

<u>Current Students</u>
Dane Christie – *Undergraduate student (CCNY)*
Federica Pozzi - *Graduate Student (Metropolitan Museum of Art)*
Francis Taplin – *Graduate student (John Jay)*
Peter Decuzzi – *Graduate student (John Jay)*
Michelle Miranda – *Graduate student (John Jay)*
Kathryn Luppino - *Undergraduate student (CCNY)*
Yi Pan – *Graduate student (CCNY)*

<u>Former Students</u>
Dr. Richard Livingstone – *Graduate student*
Loes Vermeij – *Undergraduate student*
Elizabeth Sefton – *Undergraduate student, WVU*
Chara Themistokleous – *Undergraduate student*
Faiza Anwar – *Graduate student*

<u>Funding</u>
Department of Justice (Award Number: **2009-DN-BX-K185**)
Center for Exploration of Nanostructures
in Sensors and Energy Systems (CENSES)