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DEPARTMENT OF CHEMISTRY & CHEMICAL BIOLOGY

INDIANA UNIVERSITY–PURDUE UNIVERSITY

School of Science
Indianapolis

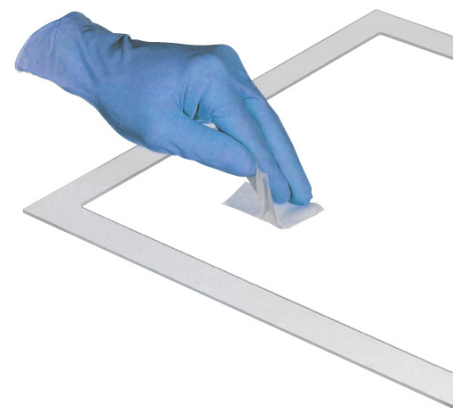
Fieldable, Dual-Technique Assay for the Analysis of Organophosphorus Compounds for Environmental and Chemical Defense Applications

Sarah Dowling and Nicholas Manicke

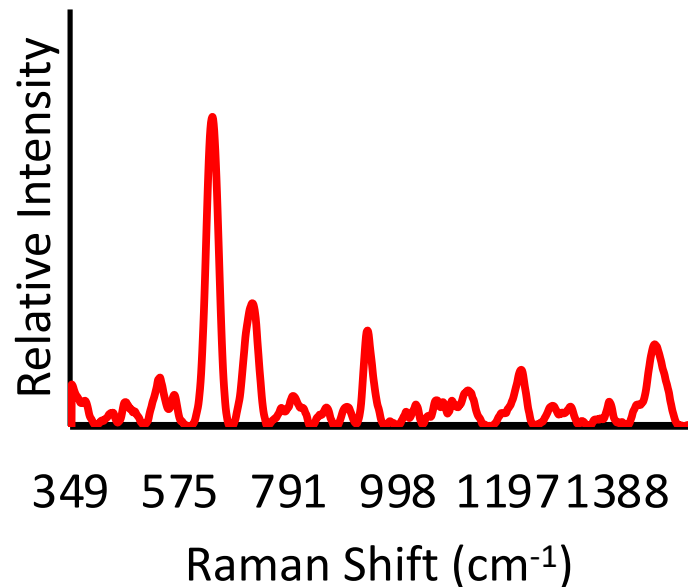
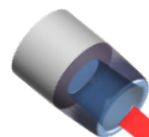
IUPUI Department of Chemistry & Chemical Biology

ASMS 2021: TOH am

Overview

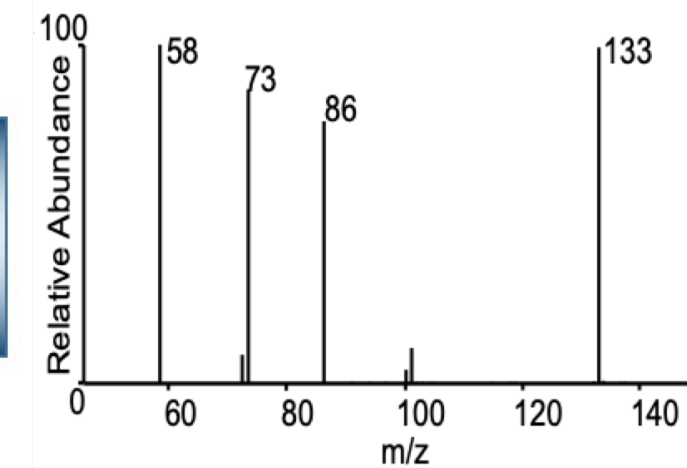
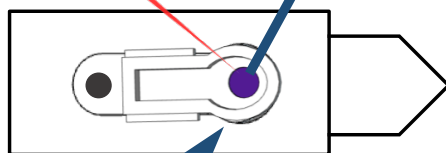


Laser



Field Testing by SERS

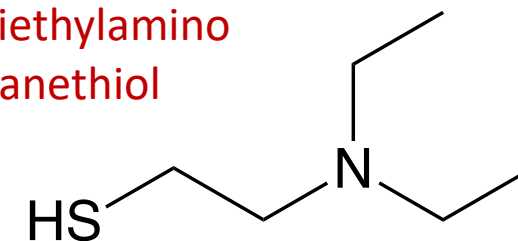
Chemical Analysis Cartridge



Automated Mass Spectrometry

Identification

2-diethylamino
ethanethiol



Organophosphorus Compounds

- Used as insecticides, medications, and nerve agents
- Inhibit esterase enzymes

Occupational Safety and Health Administration Nerve Agents Guide

Low Dose	Medium Dose	High Dose
<ul style="list-style-type: none">• Runny nose• Pupil contraction• Headache• Slurred speech• Chest pains	<ul style="list-style-type: none">• More pronounced symptoms• Coughing• Breathing problems• Convulsions	<ul style="list-style-type: none">• Immediate convulsions• Shut down of nervous and respiratory system• Death from suffocation

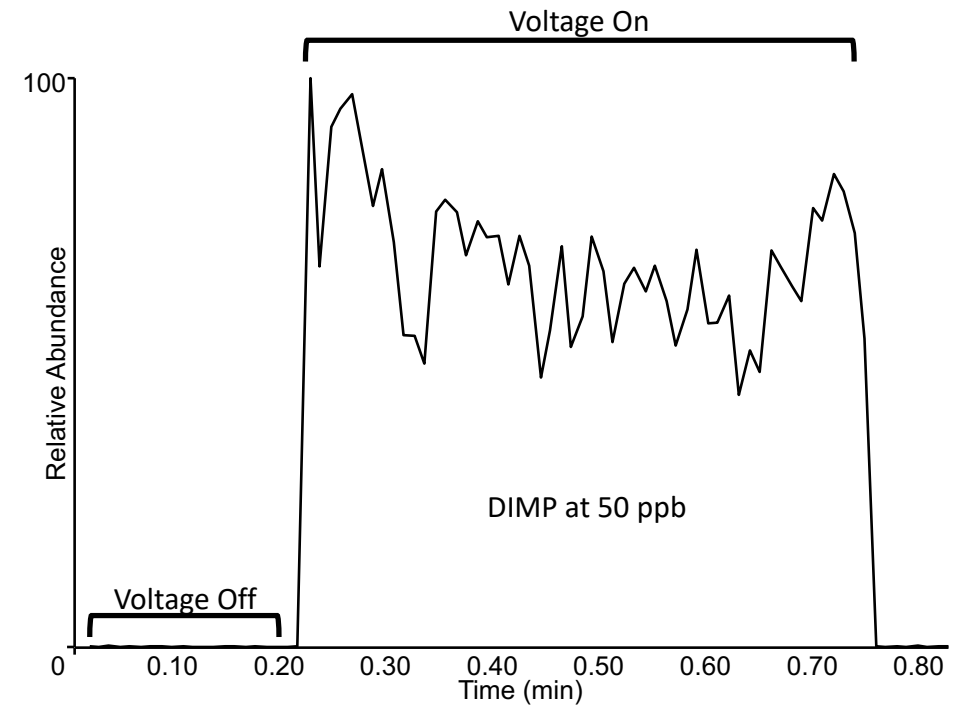
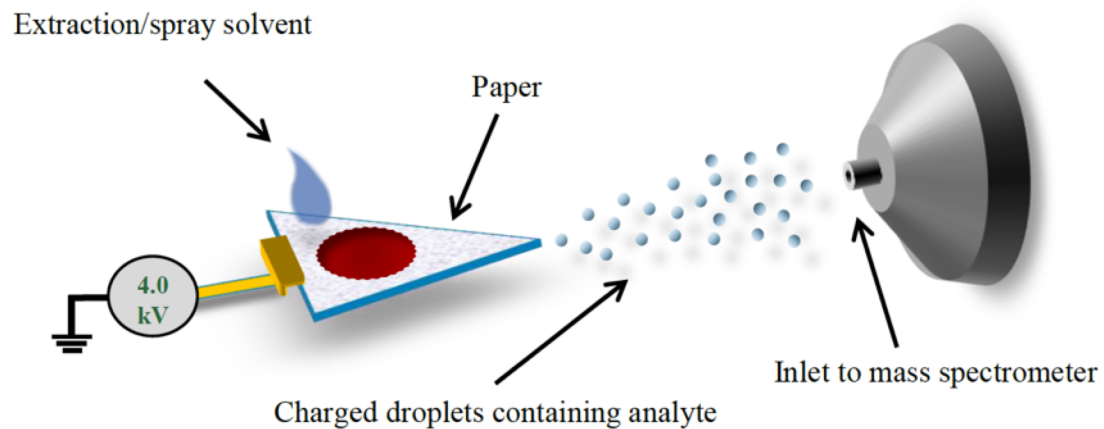


The Guardian



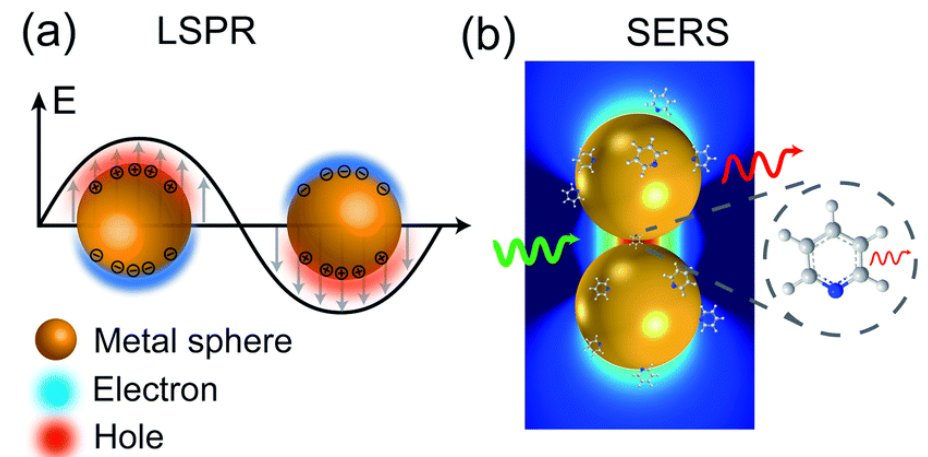
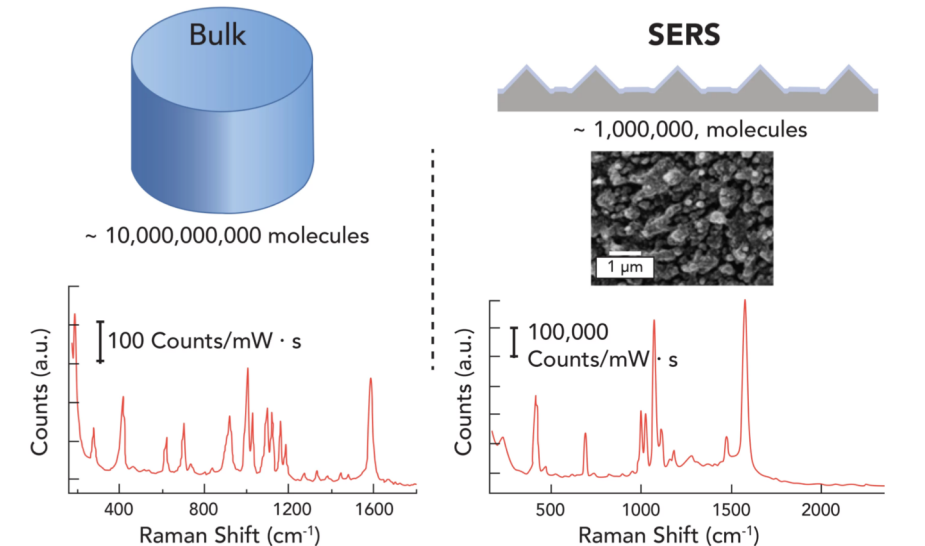
Desmond Boylan/Reuters

Paper Spray Mass Spectrometry (PS-MS)

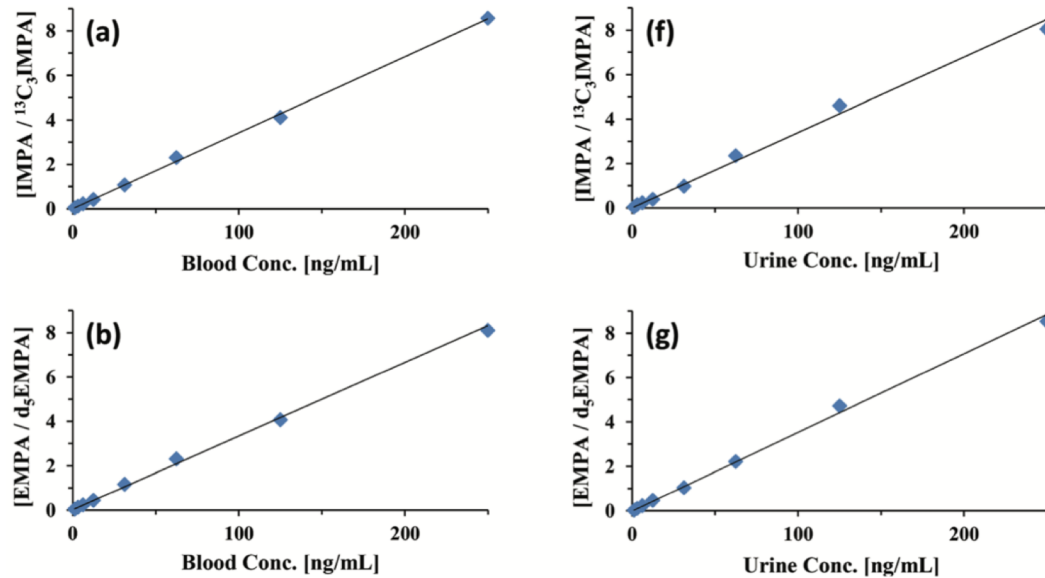


Surface Enhanced Raman Spectroscopy (SERS)

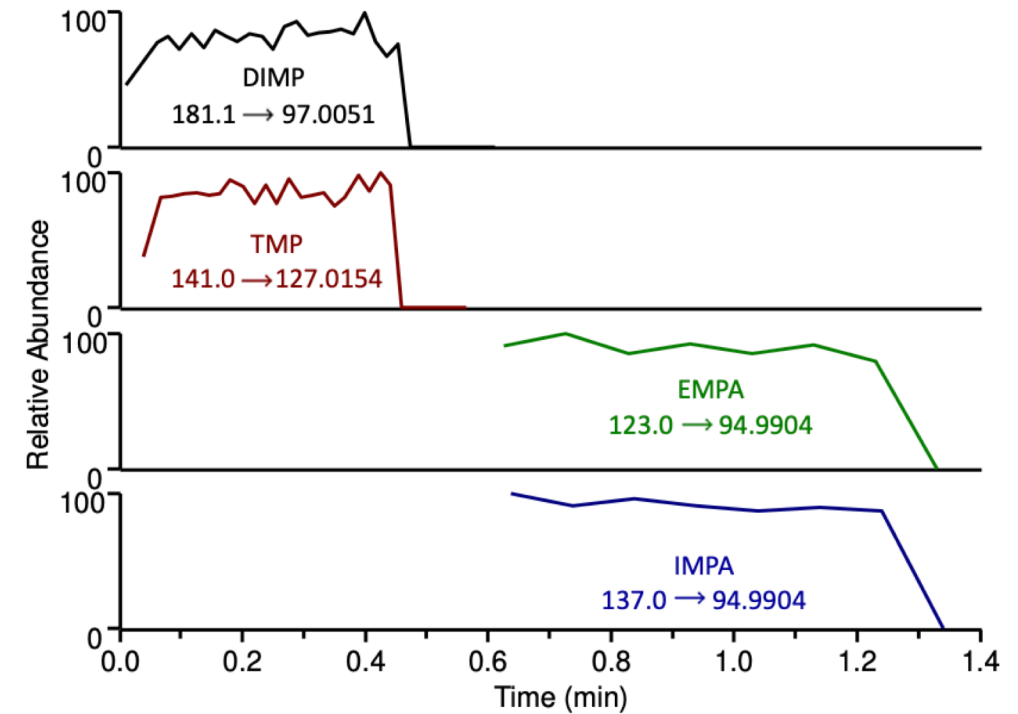
- Raman is a vibrational spectroscopic technique
- Inelastic scattering of photons
- Raman generally not sensitive
- SERS enhances Raman scattering
 - Localized surface plasmon resonance (LSPR)



Previous Work

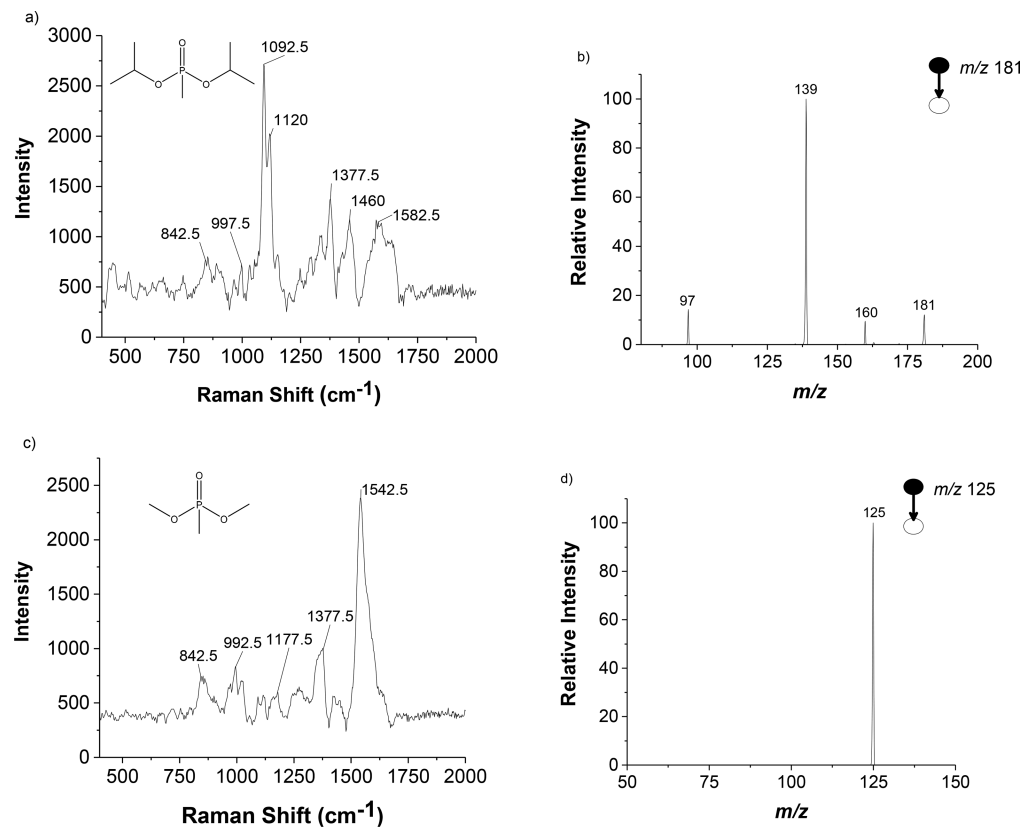


McKenna, J., et al. (2017). *Analyst*, 142(9), 1442-1451.

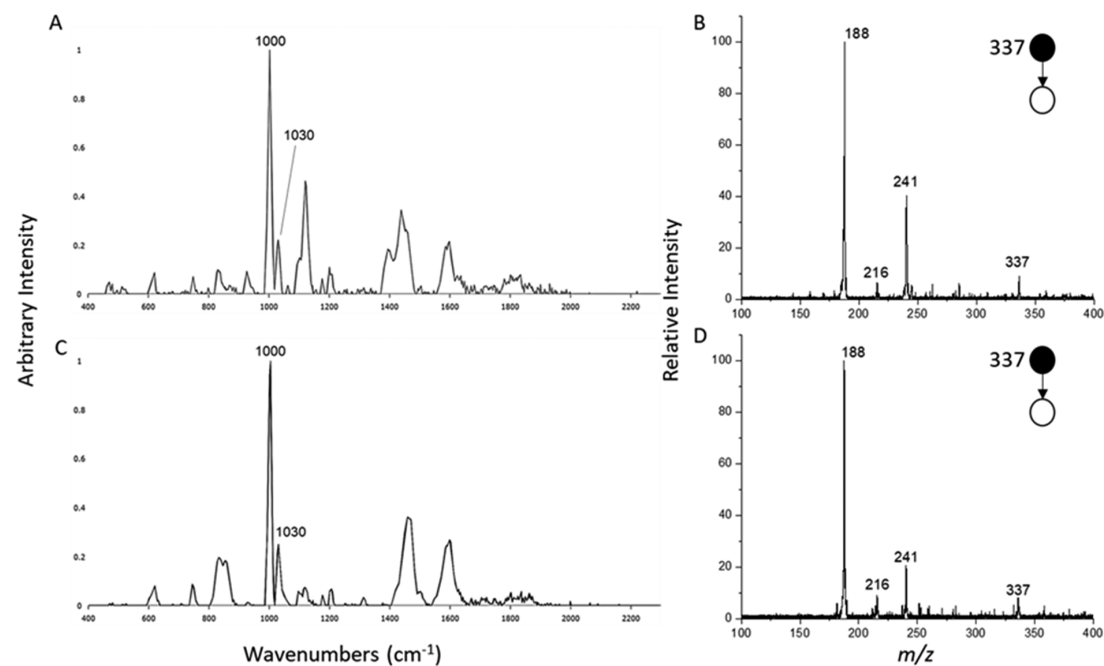


Dowling, S., et al. (2019). *Forensic Chemistry*, 100206.

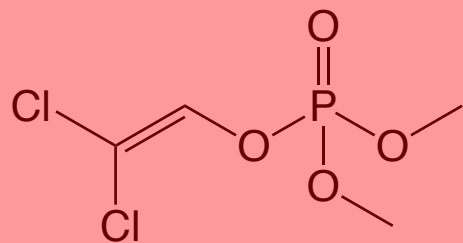
Previous Work



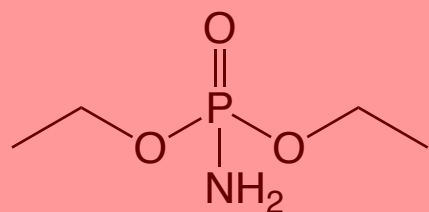
Fedick, P. W., et al. (2017) *Analytical Chemistry*, 89(20), 10973-10979.



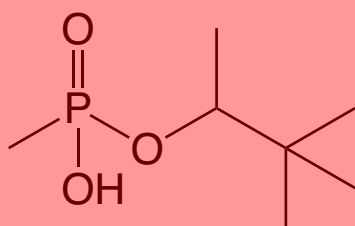
Fedick, P. W., et al. (2020). *Journal of The American Society for Mass Spectrometry*, 31(3), 735-741.



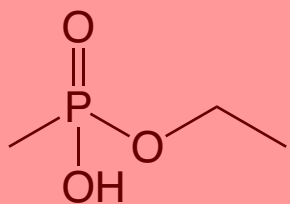
Dichlorvos



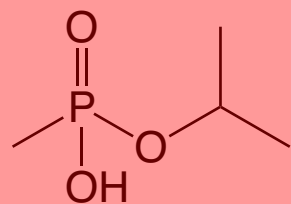
Diethyl phosphoramidate
(DEPA)



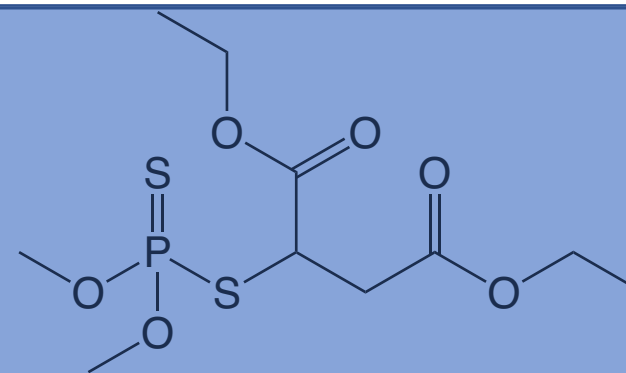
Pinacolyl
methylphosphonic acid
(PinMPA)



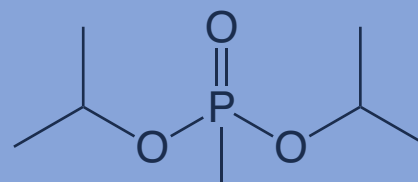
Ethyl
methylphosphonic acid
(EMPA)



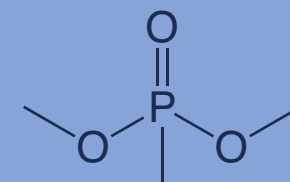
Isopropyl
methylphosphonic acid
(IMPA)



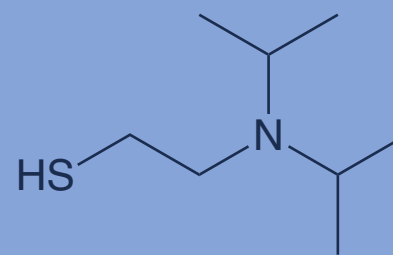
Malathion



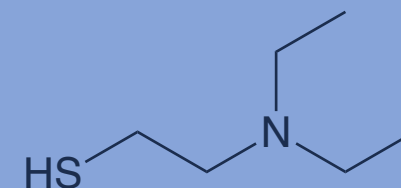
Diisopropyl
methylphosphonate
(DIMP)



Dimethyl
methylphosphonate
(DMMP)



2-(Diisopropylamino)
ethanethiol
(IDA)



2-(Diethylamino)
ethanethiol
(EDA)

Paper-Based SERS

SERS Parameters
785 nm laser
30% power
5x average
10s integration time

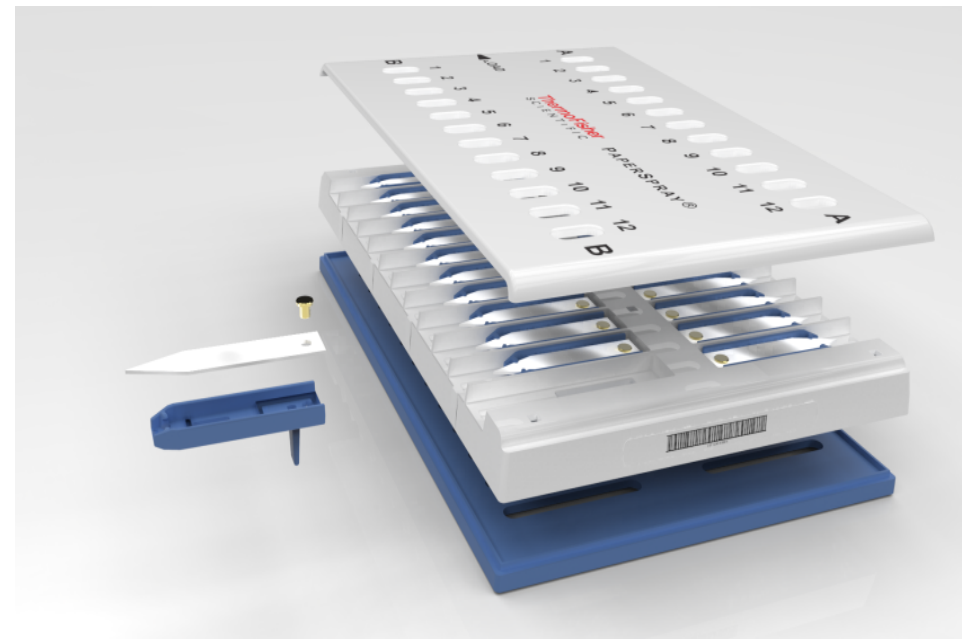
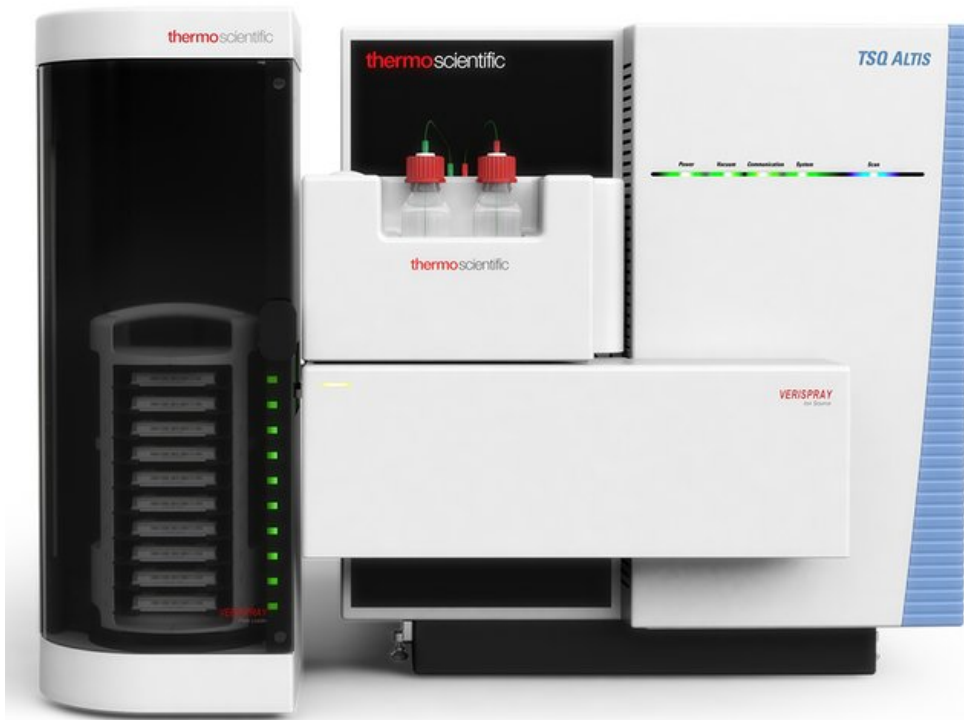
B&W Tek iRaman Plus



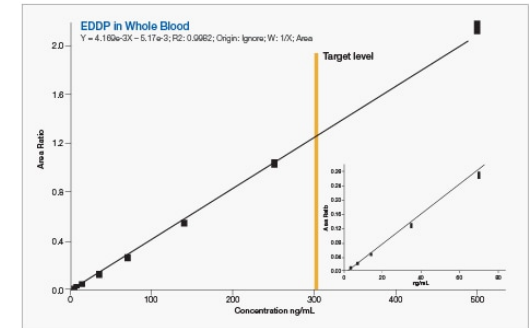
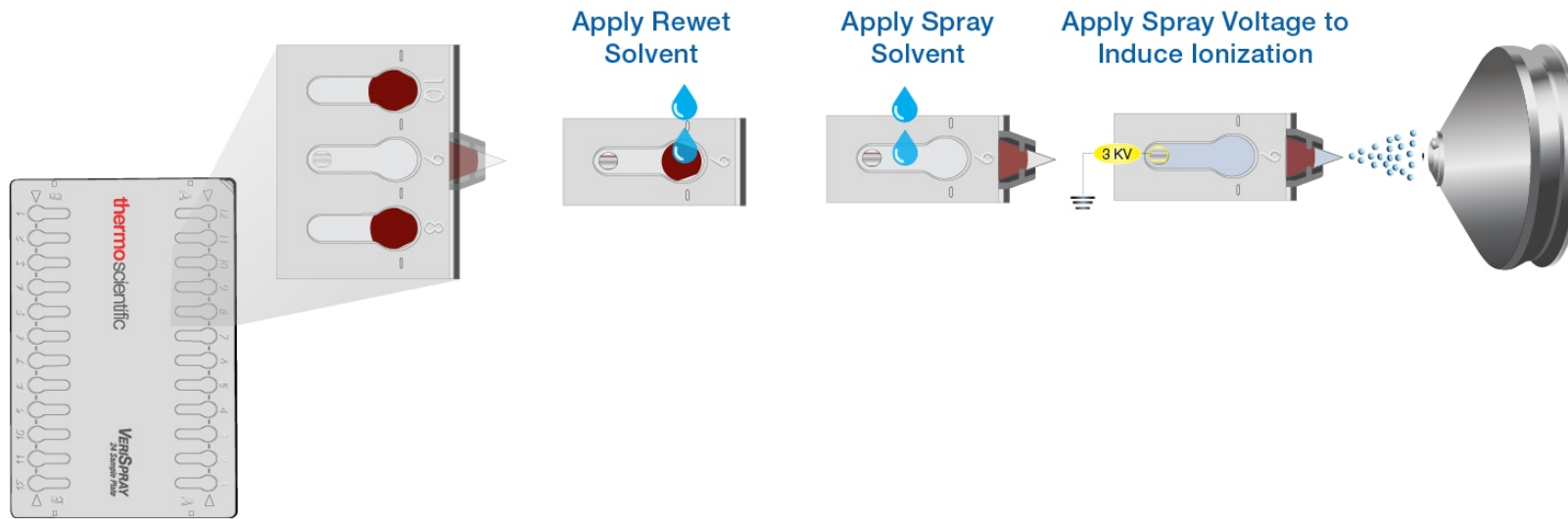
Metrohm P-SERS Paper



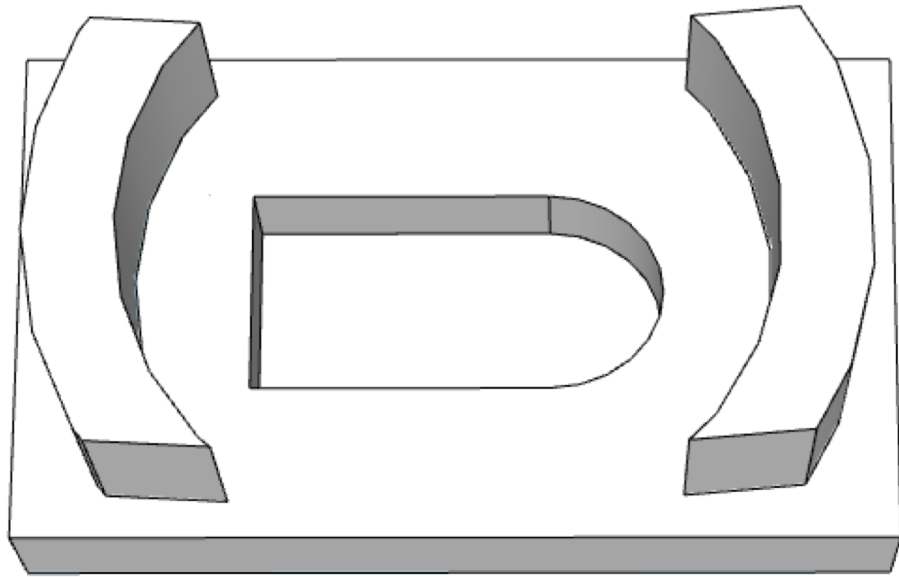
VeriSpray Paper Spray Source



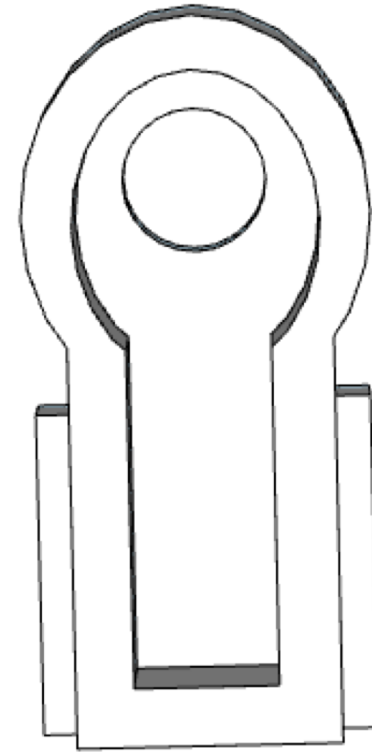
Automated Paper Spray



3D Printed Devices

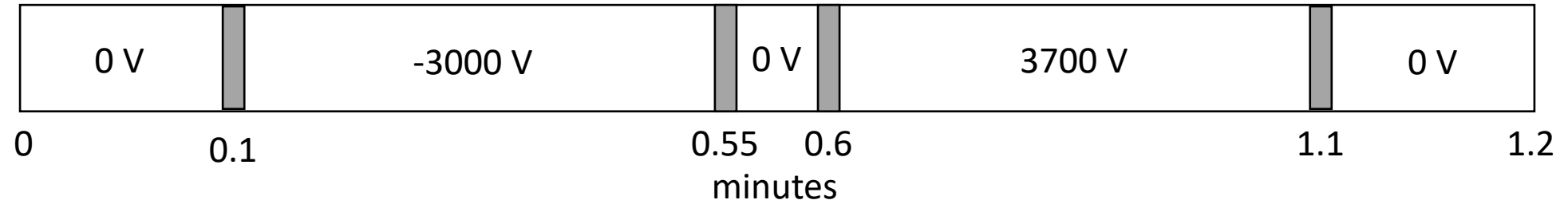


Laser Probe Holder



PS/SERS Insert

Paper Spray Parameters



Level	Concentration (ng)	Concentration (ppm)
1	75	25
2	37.5	12.5
3	18.75	6.25
4	9.375	3.13
5	4.6875	1.56

3 uL ISTD spotted ON TOP
MeOH with 0.1% FA solvent

Sample In-Field Workflow



Fig. 1 pSERS strips



Fig. 2 pSERS punch in insert for sample application

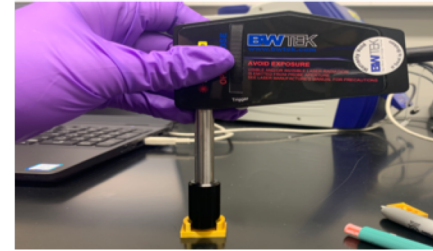


Fig. 3 SERS probe and insert holder

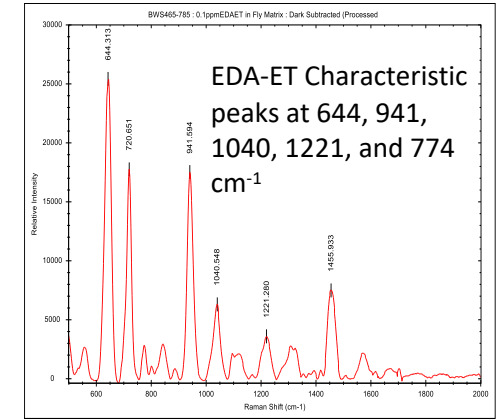


Fig. 4 SERS Spectrum



Fig. 5 Insert inside of VeriSpray sample plate



Fig. 6 Plates loaded into VeriSpray automated source system on Altis MS

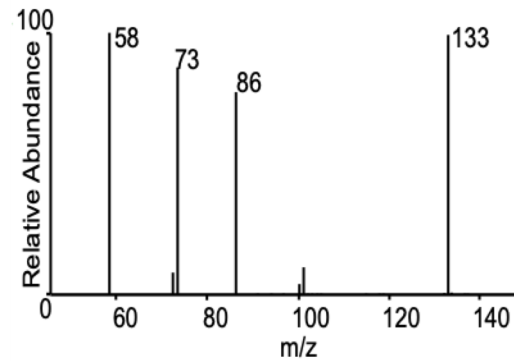
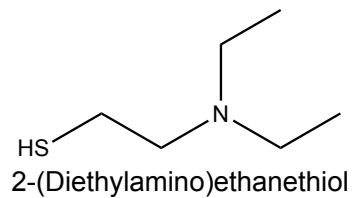
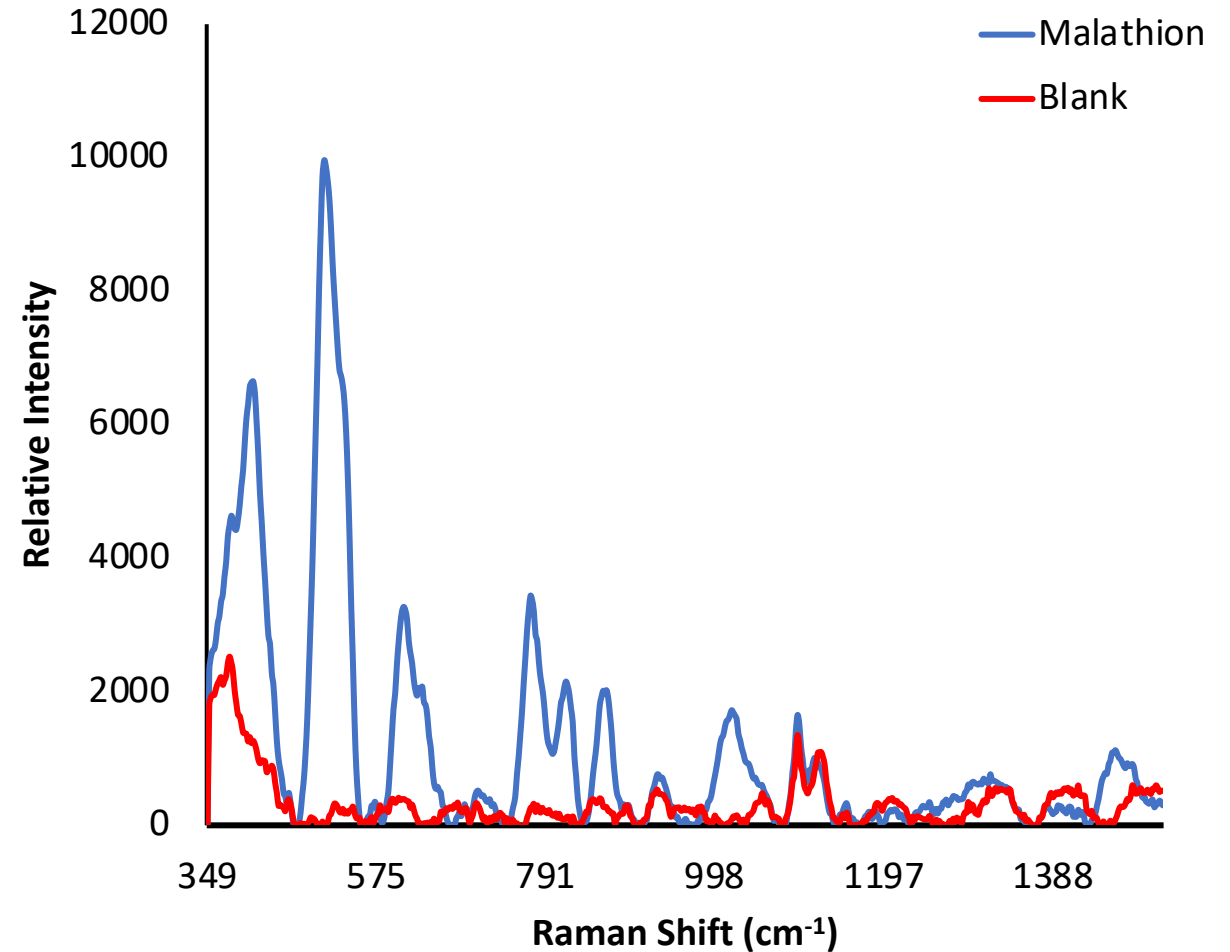
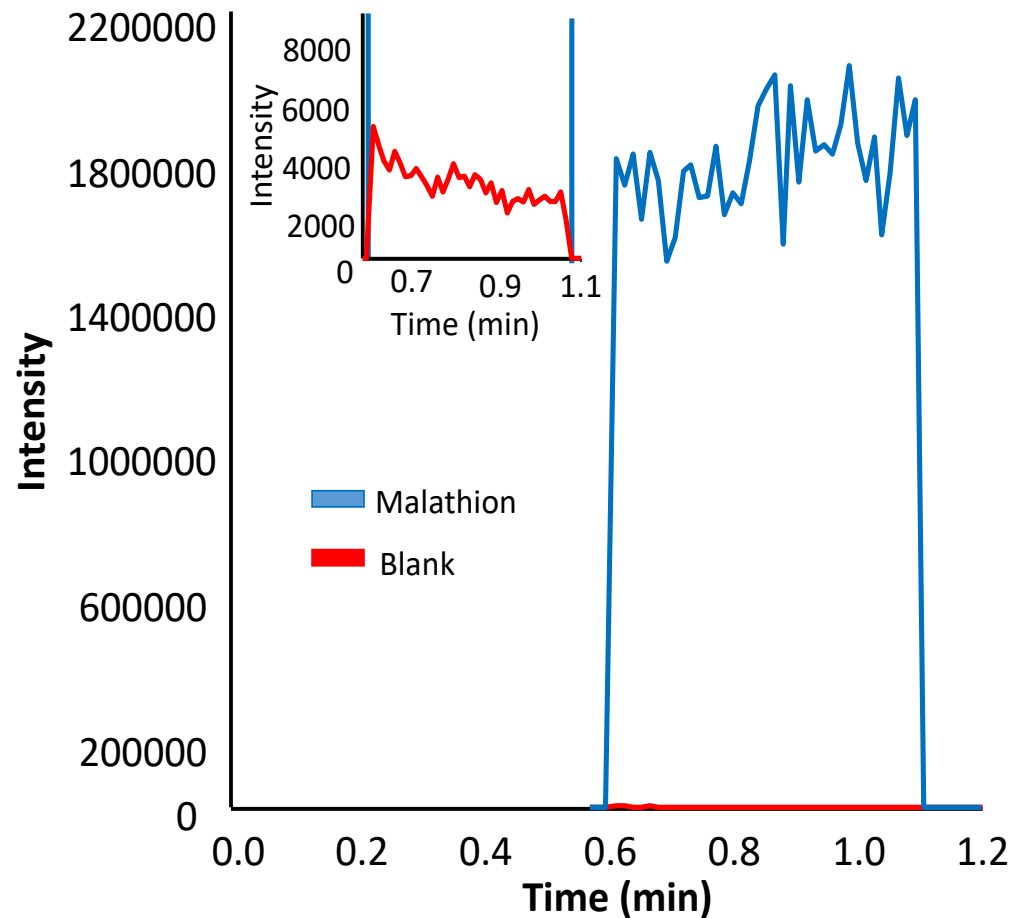


Fig. 7 PS-MS analysis

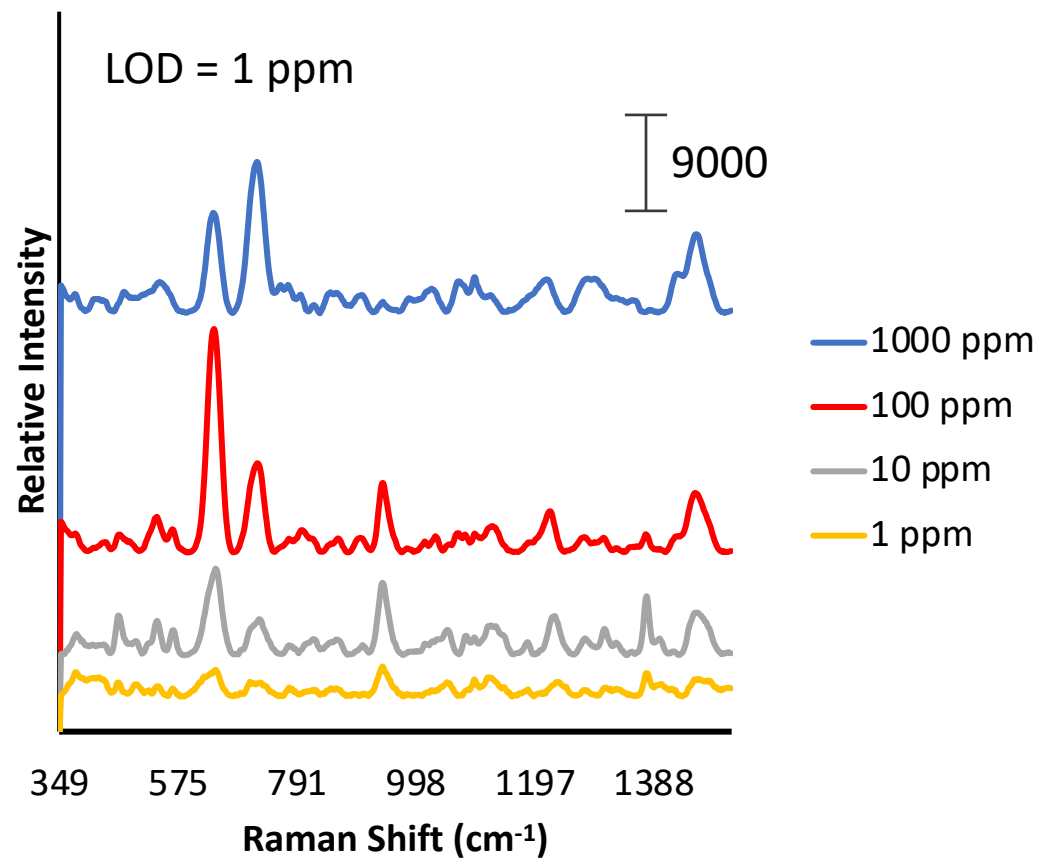
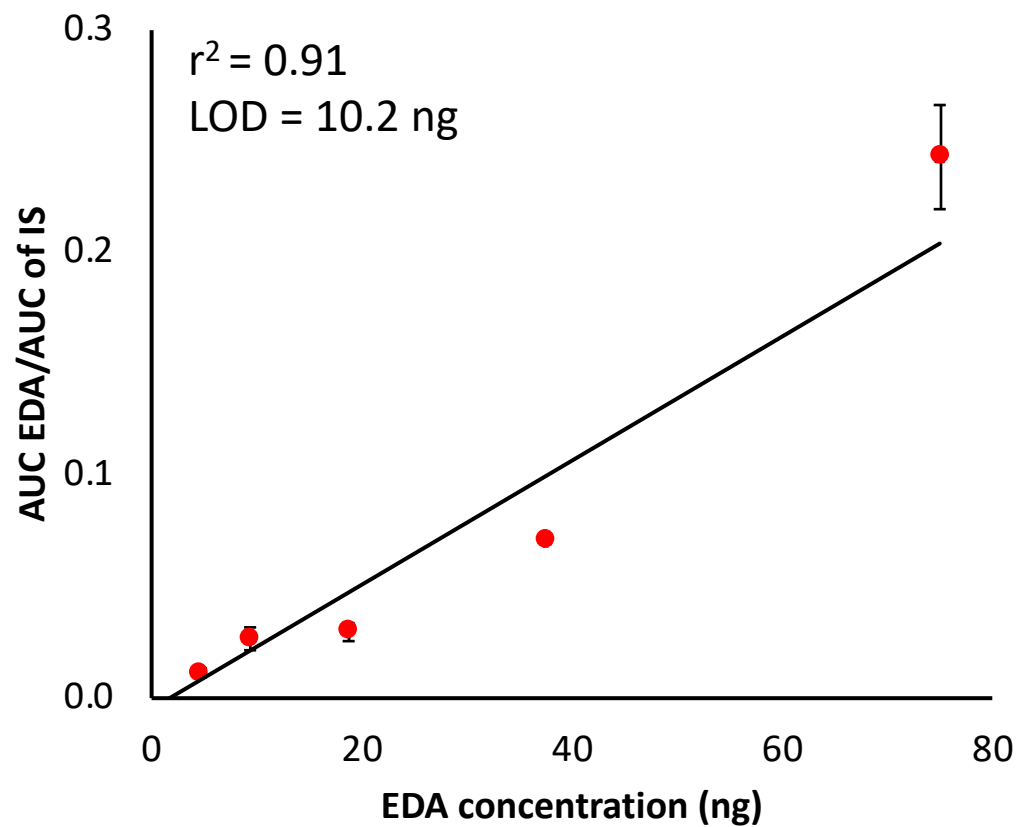
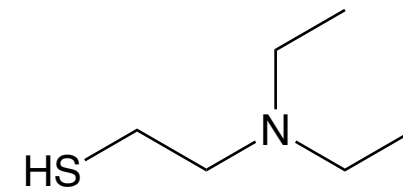


Sample analyzed with SERS then PS

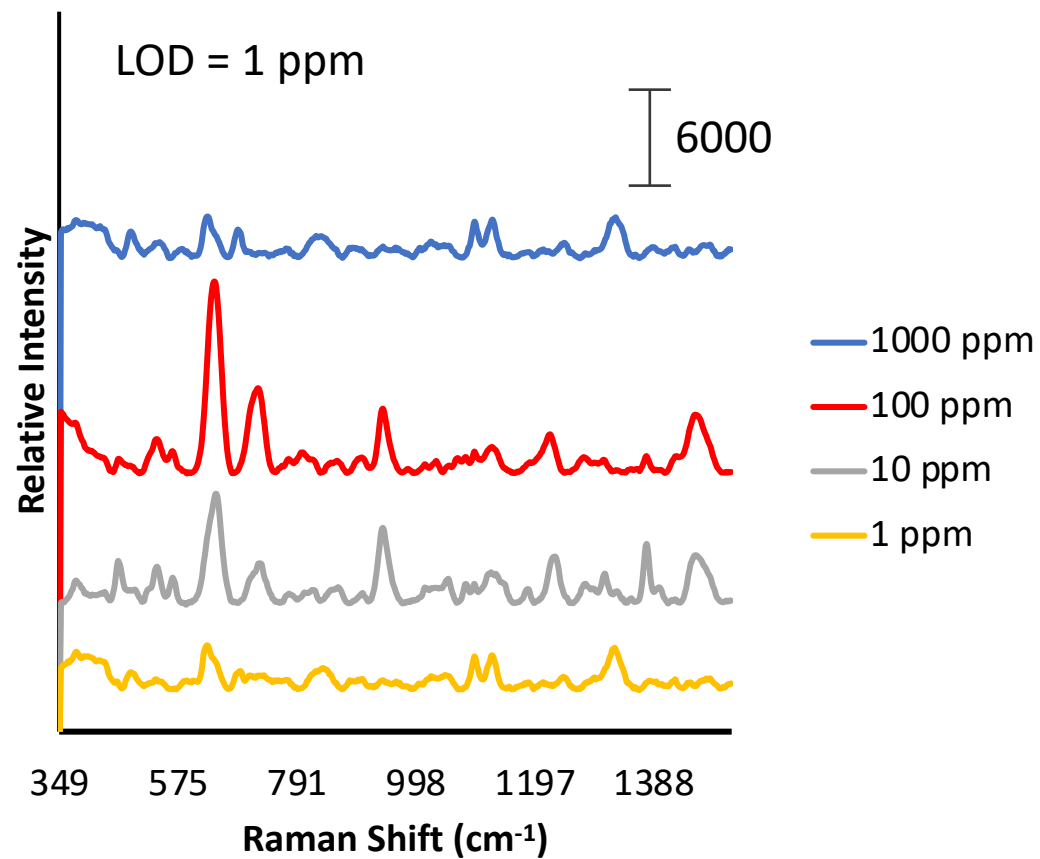
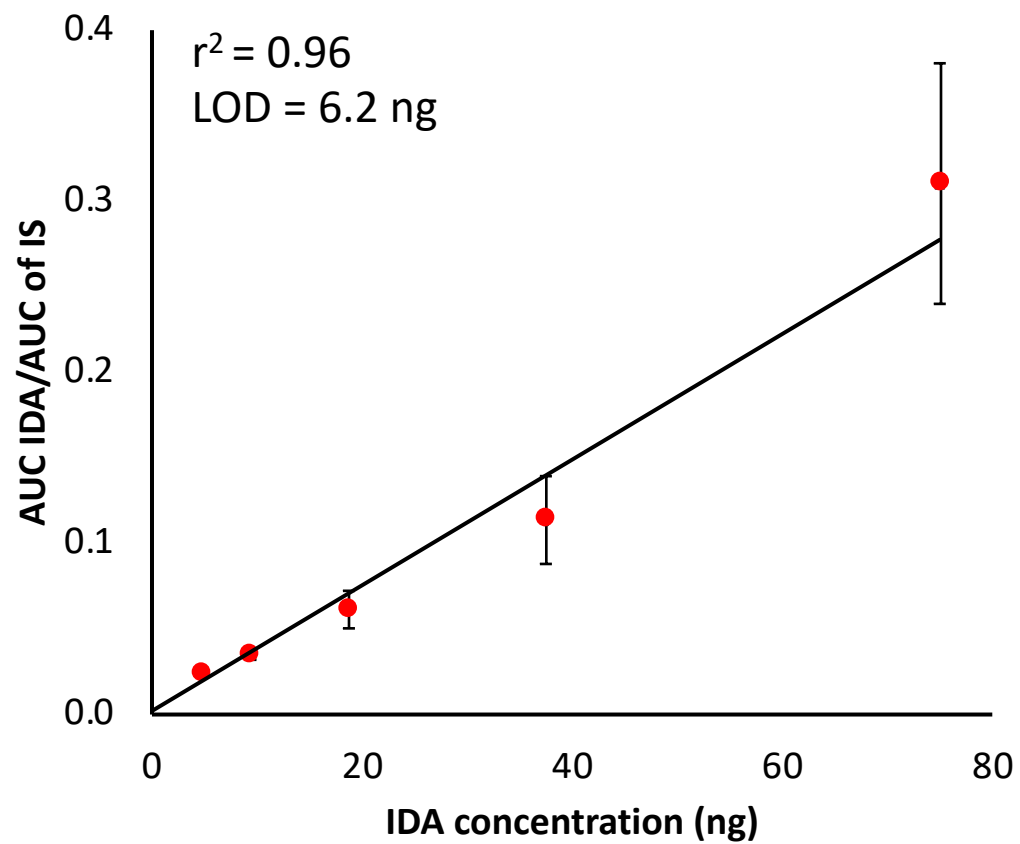
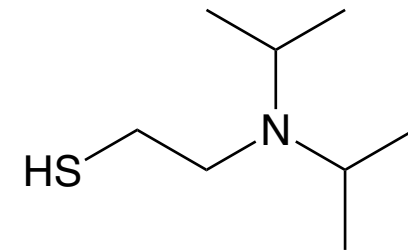
Malathion (10 ppm - 30 ng)



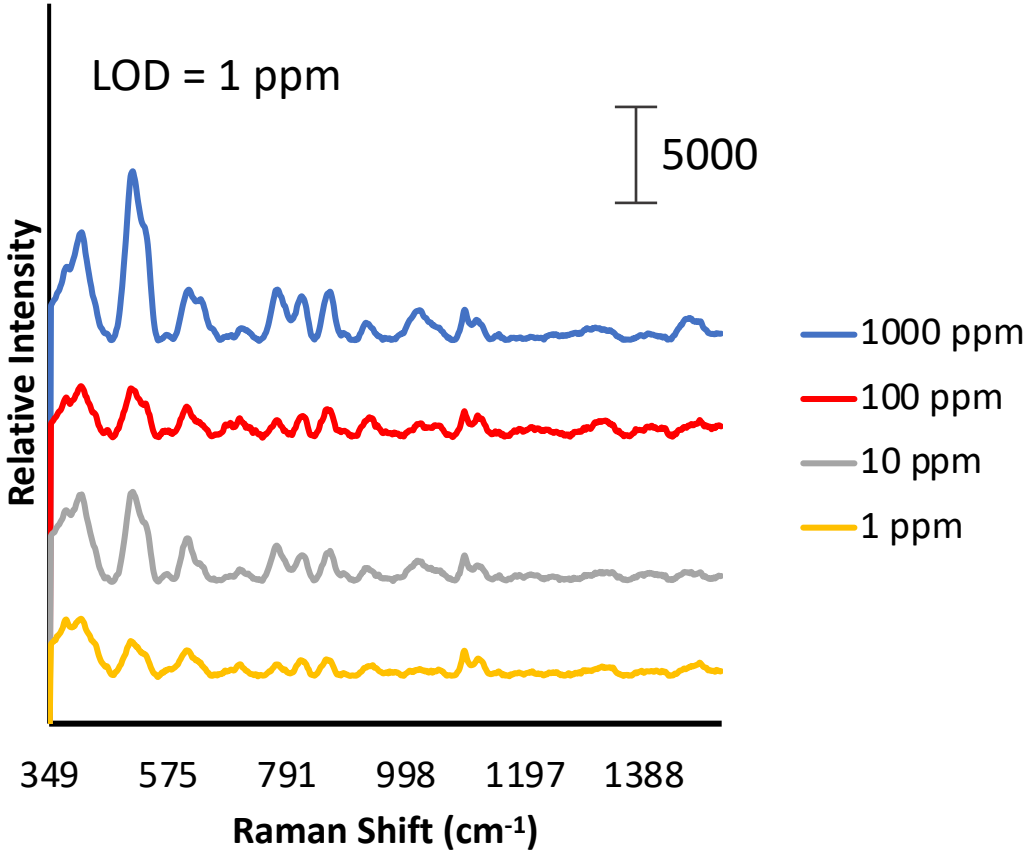
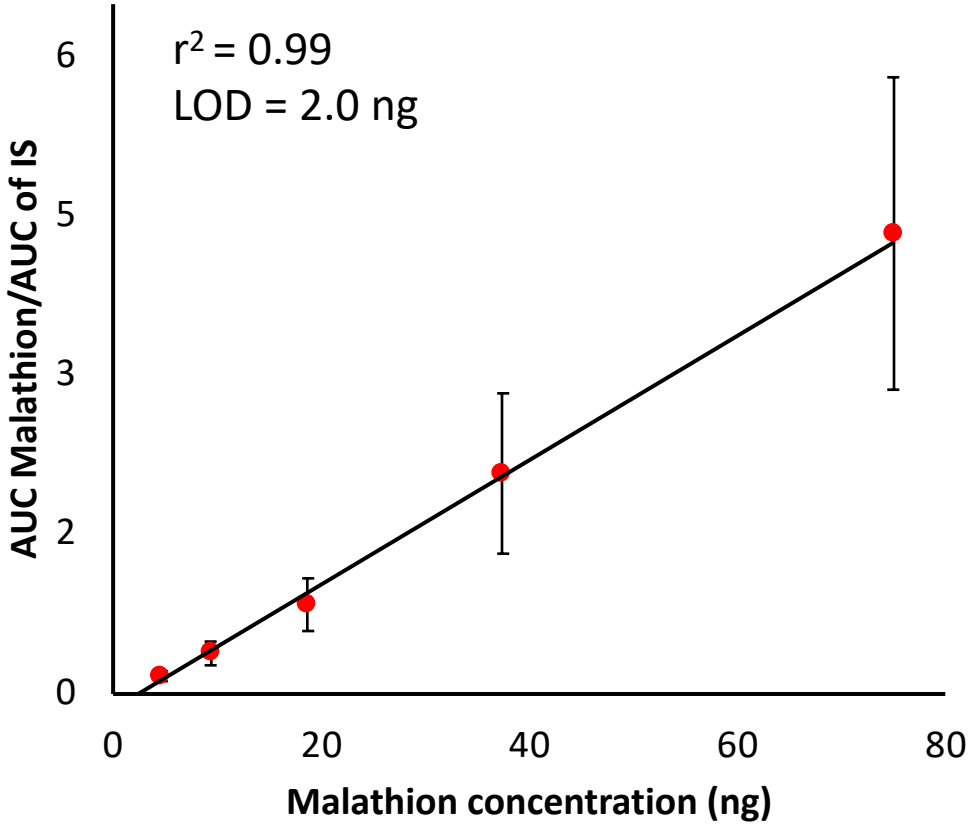
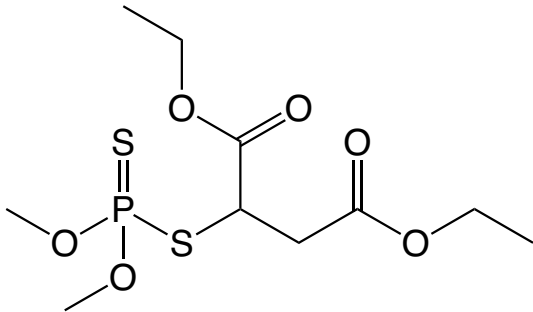
EDA



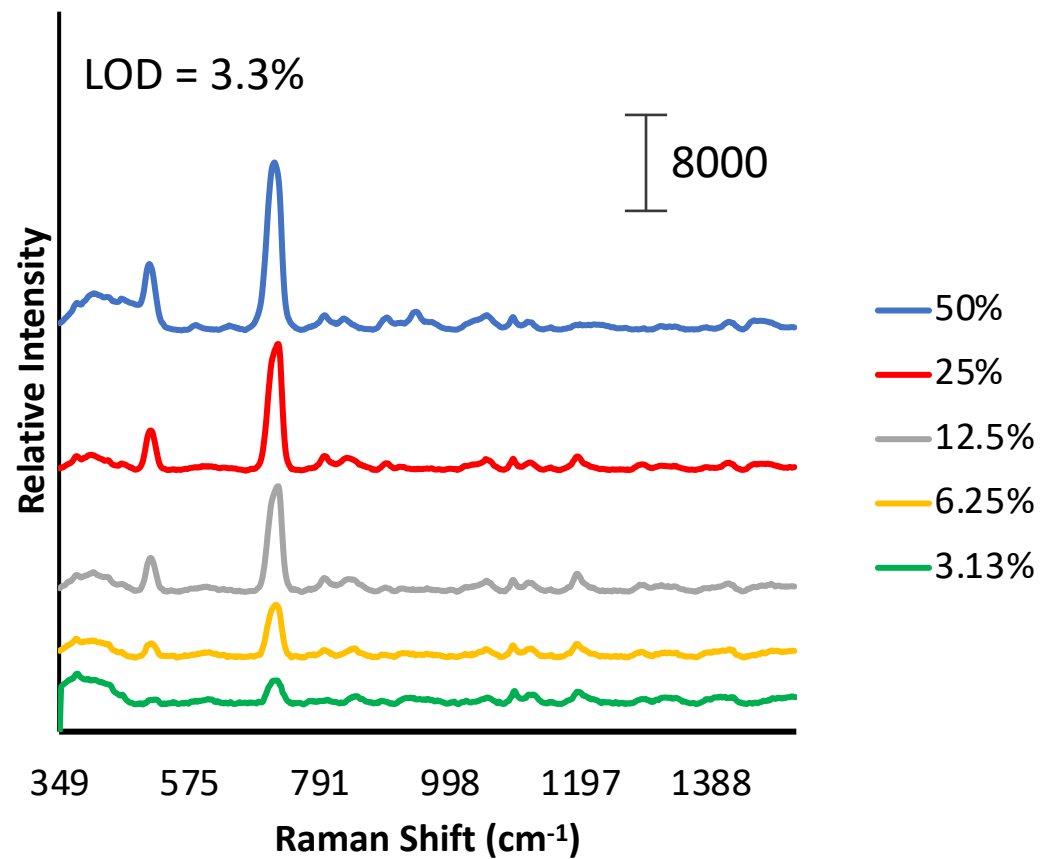
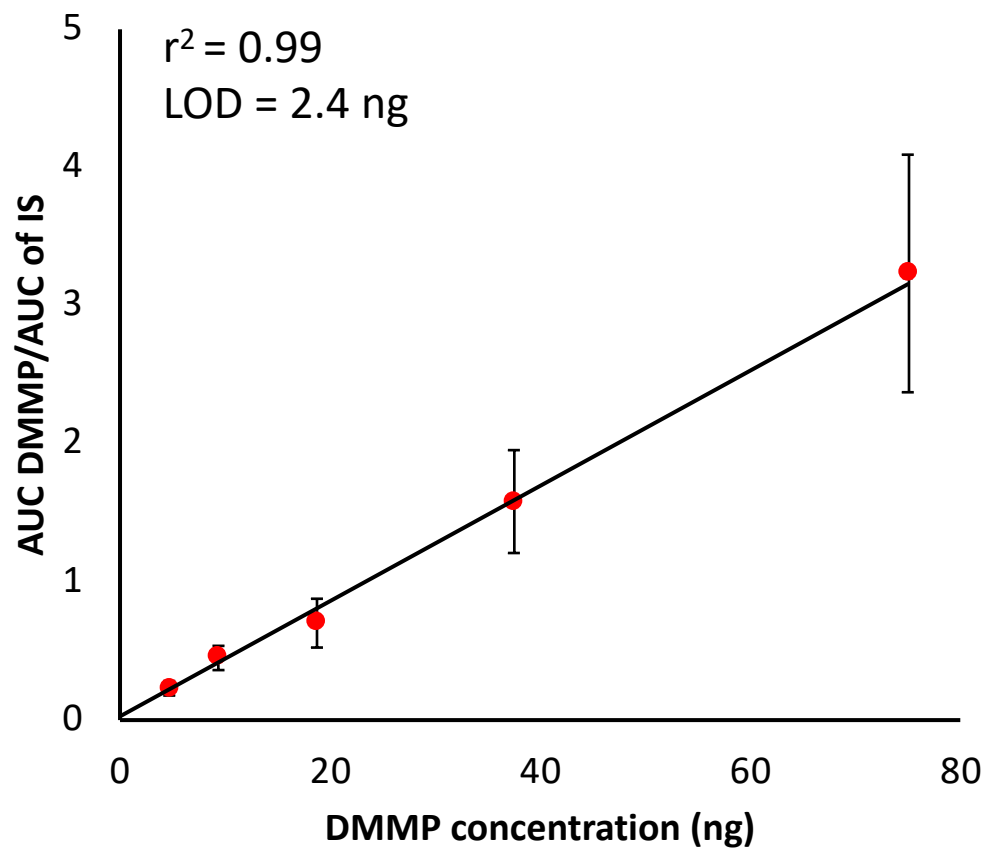
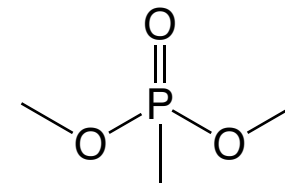
IDA



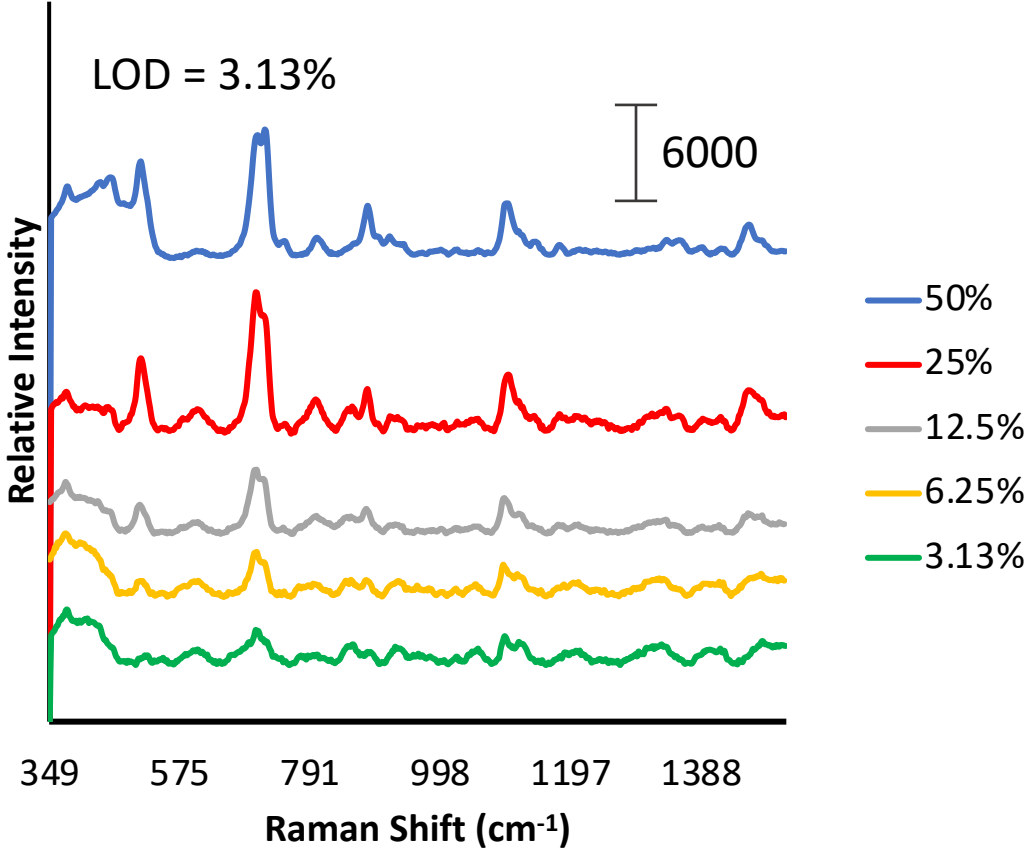
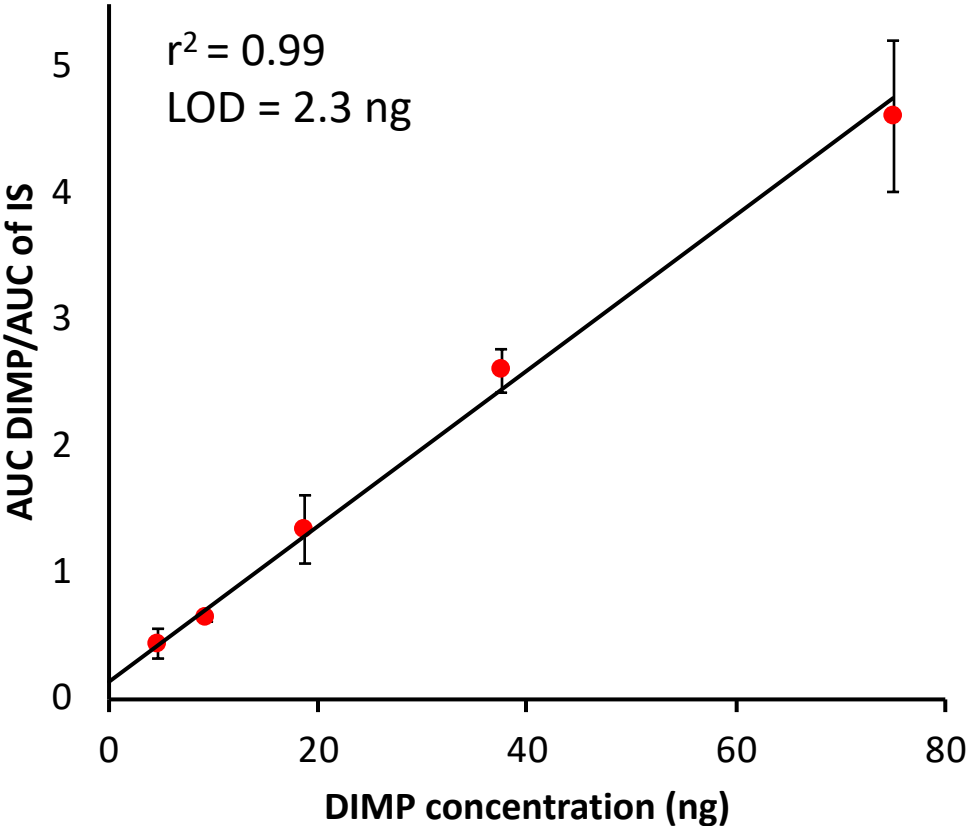
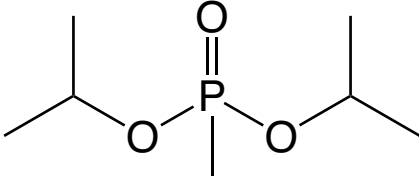
Malathion



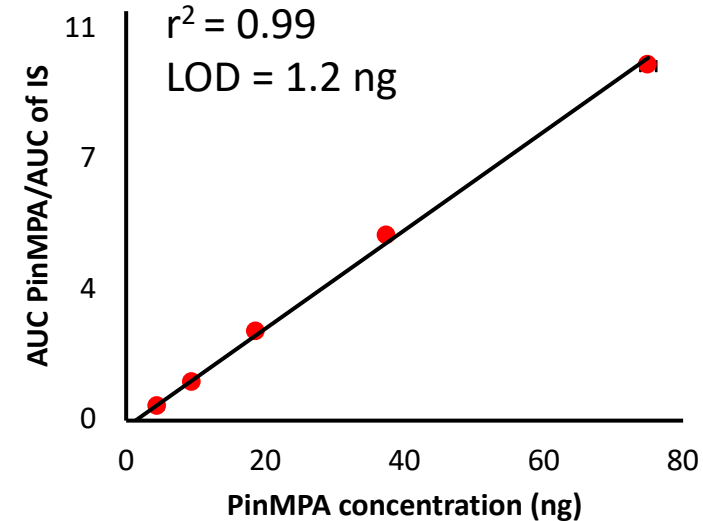
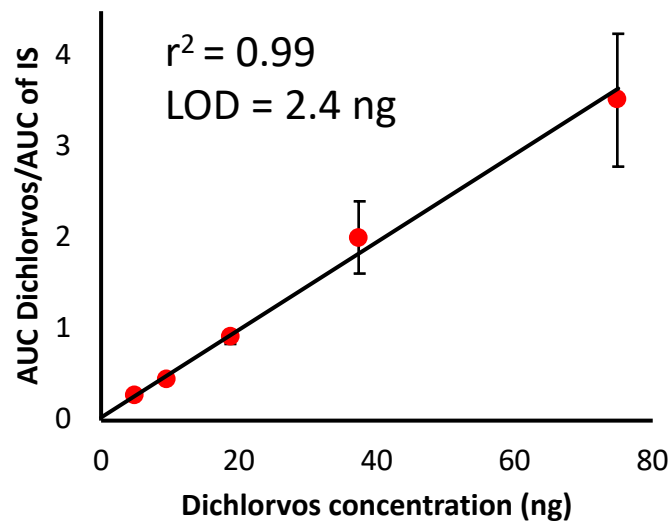
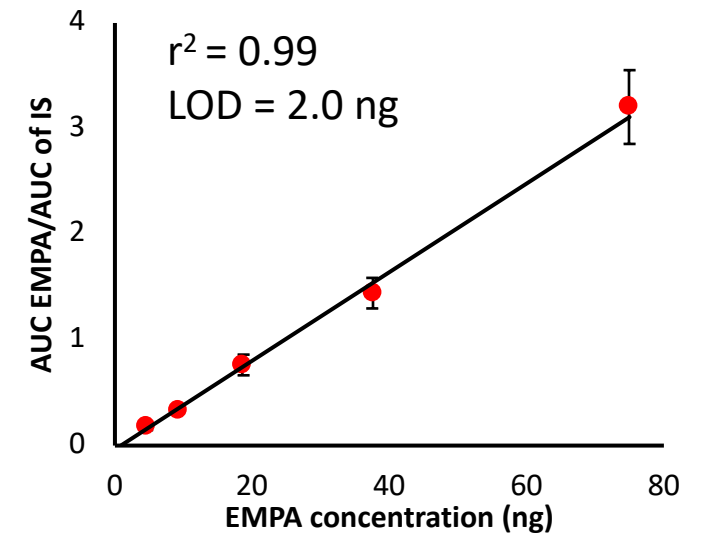
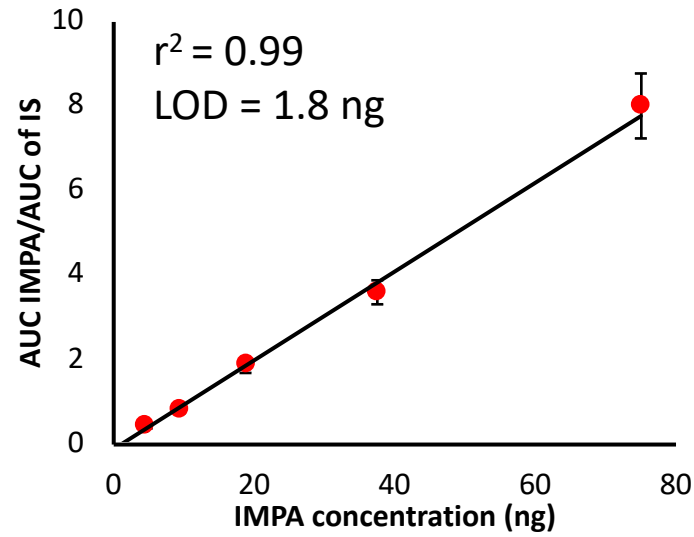
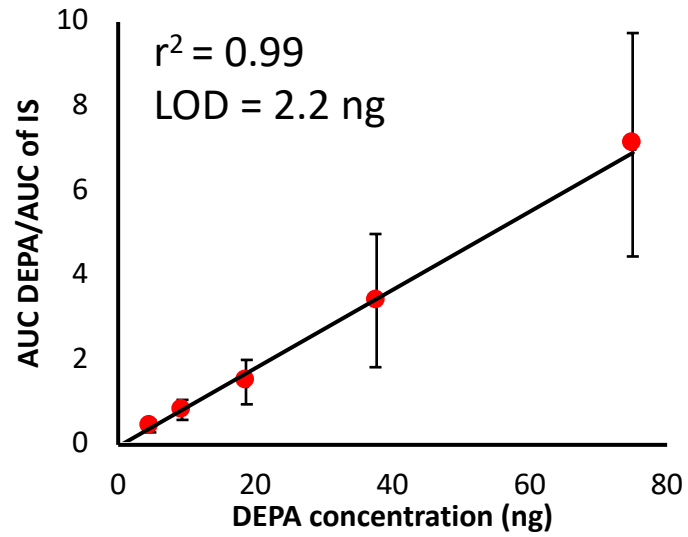
DMMP



DIMP

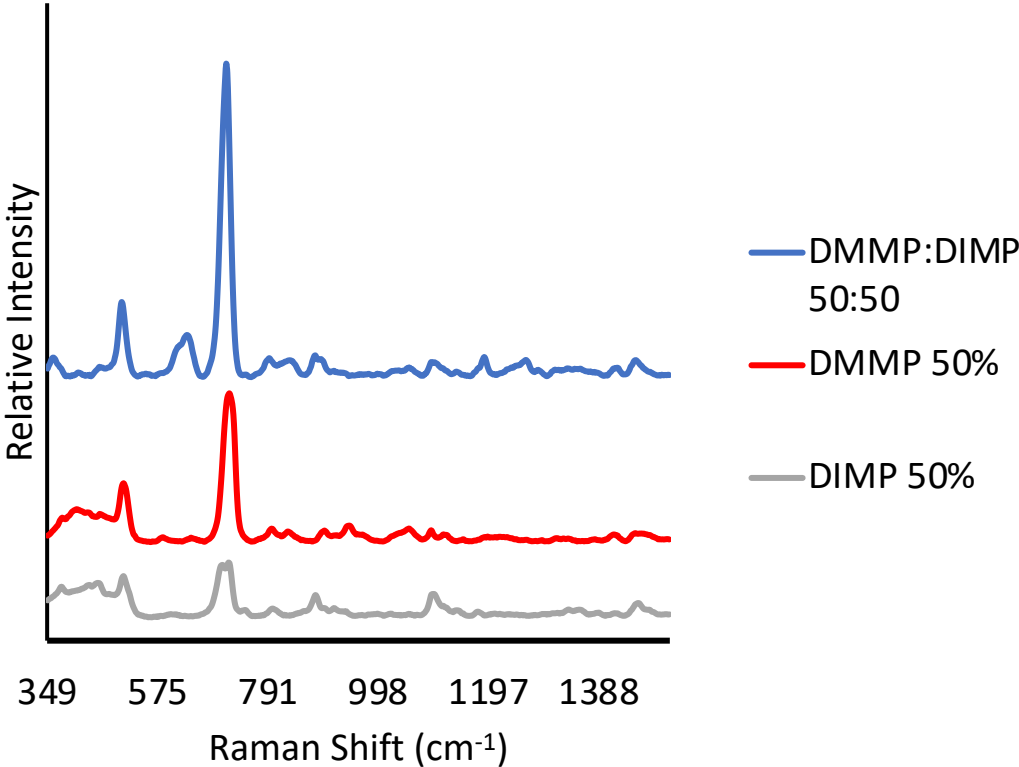


Analytes not detected with SERS

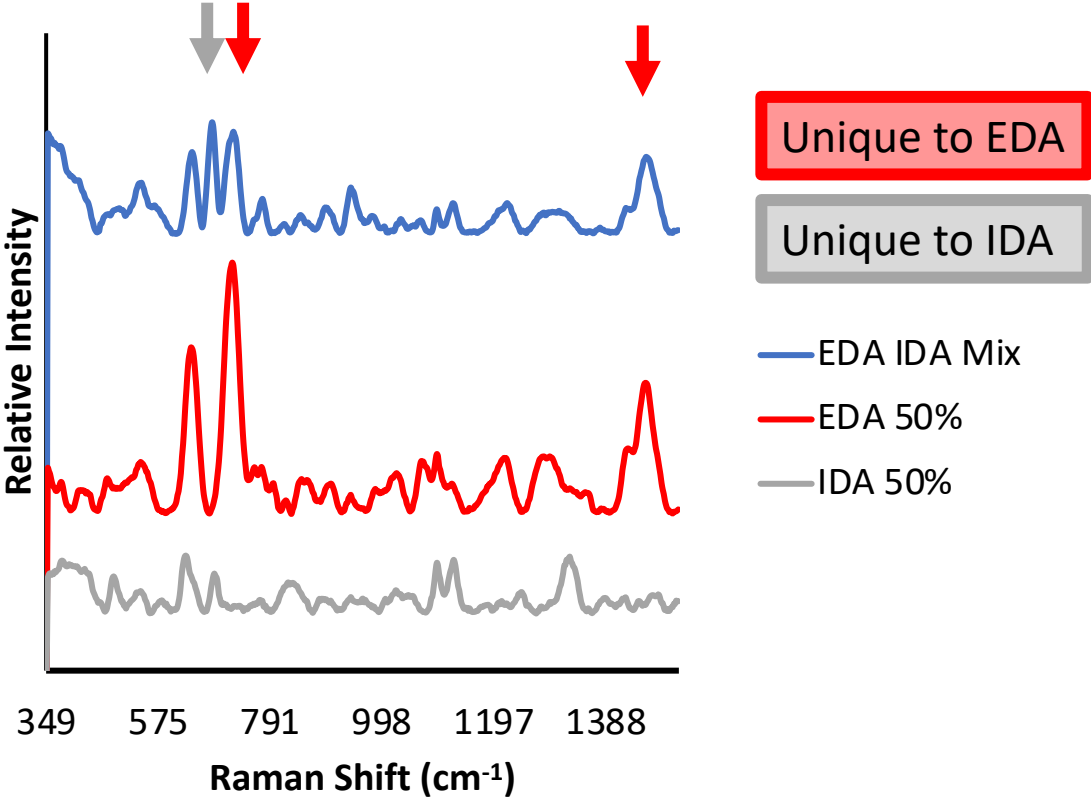


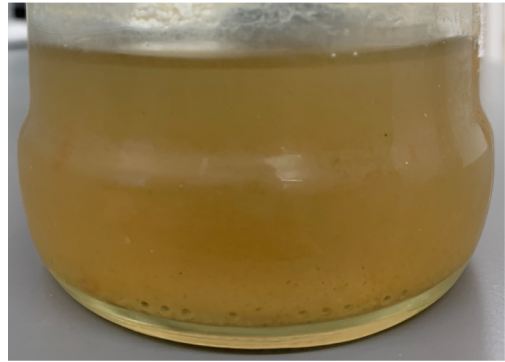
Mixtures

DIMP and DMMP Mixture



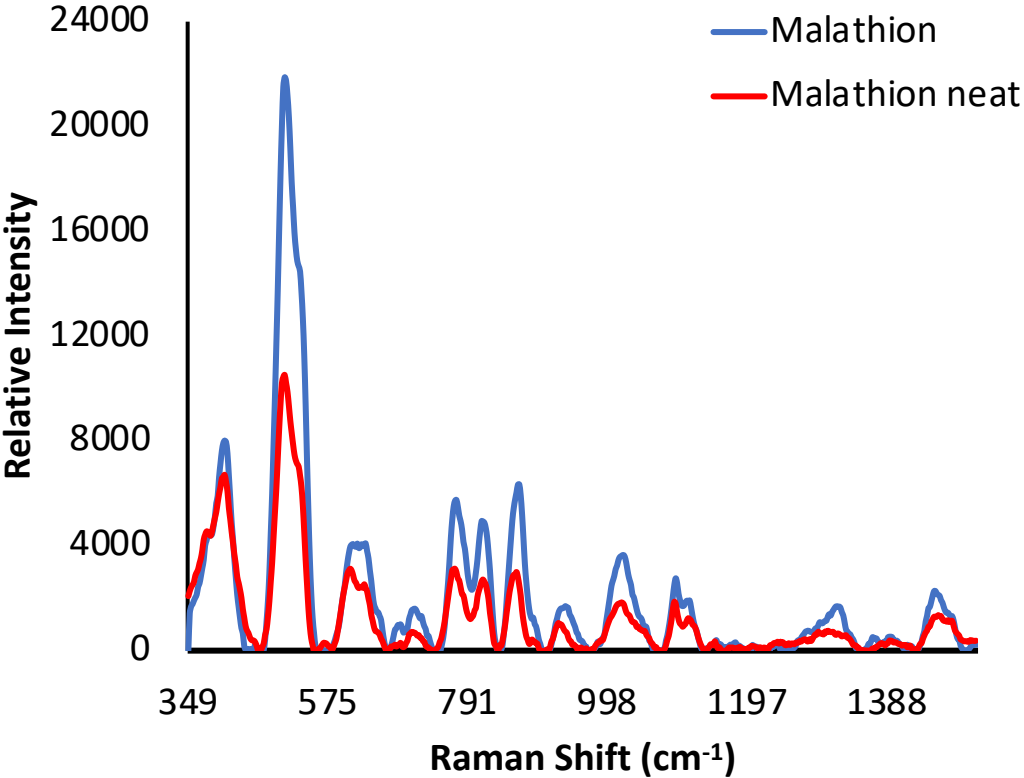
EDA and IDA Mixture



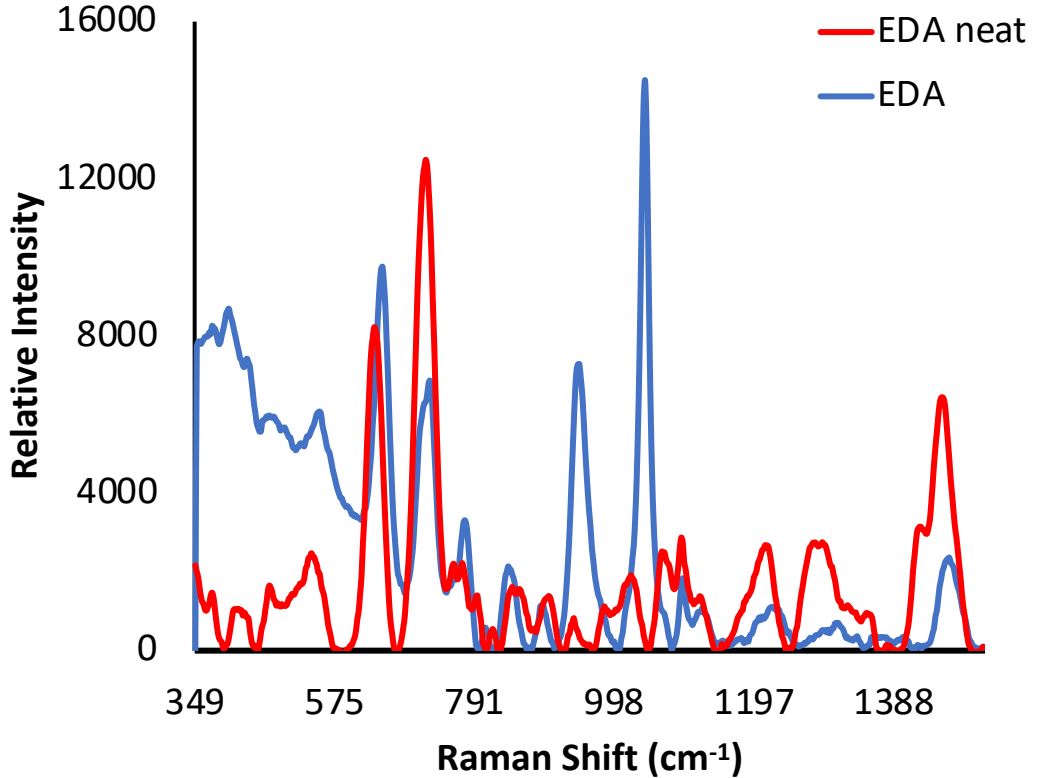


River Water

Malathion in River Water



EDA in River Water



Conclusions/future directions

- Developed of a dual-technique assay to detect organophosphorus compounds
- Determined LODs for compounds using PS and SERS
- 3D printed insert for facilitating the transfer between methods
- Future work will focus on:
 - Modifying the substrate surface with an affinity-based treatment to improve the SERS performance for the molecules that were not detected
 - Developing a 3D printed sampling apparatus for wiping chemicals off surfaces
 - Use of a portable MS

Acknowledgements

- Manicke Research Group
- Defense Advanced Research Project Agency (DARPA)
- IUPUI Department of Chemistry and Chemical Biology



(Left to right)

Back: Tracy Nguyen, Sarah Dowling, Hannah Zimmerman, Greta Ren

Front: Christine Skaggs, Nick Manicke, Magnus Rydberg

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