Remote Raman & Fluorescence Capabilities for Chemical Detection at University of Hawaii

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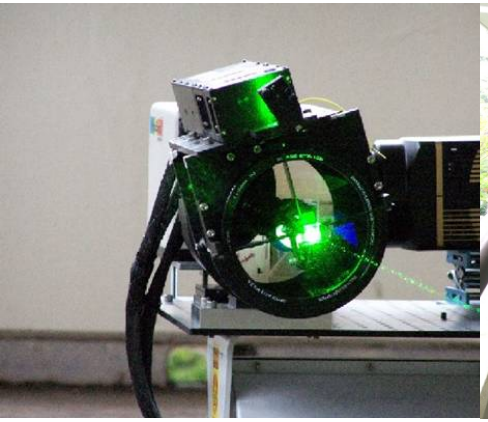
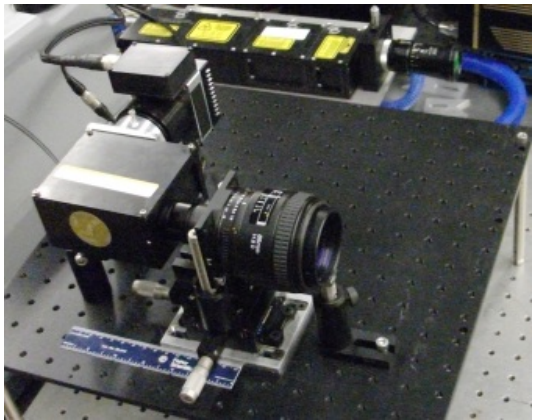
* Daytime Operation
* Long Detection Range (no sample collection)
* Fast Response
* Portable

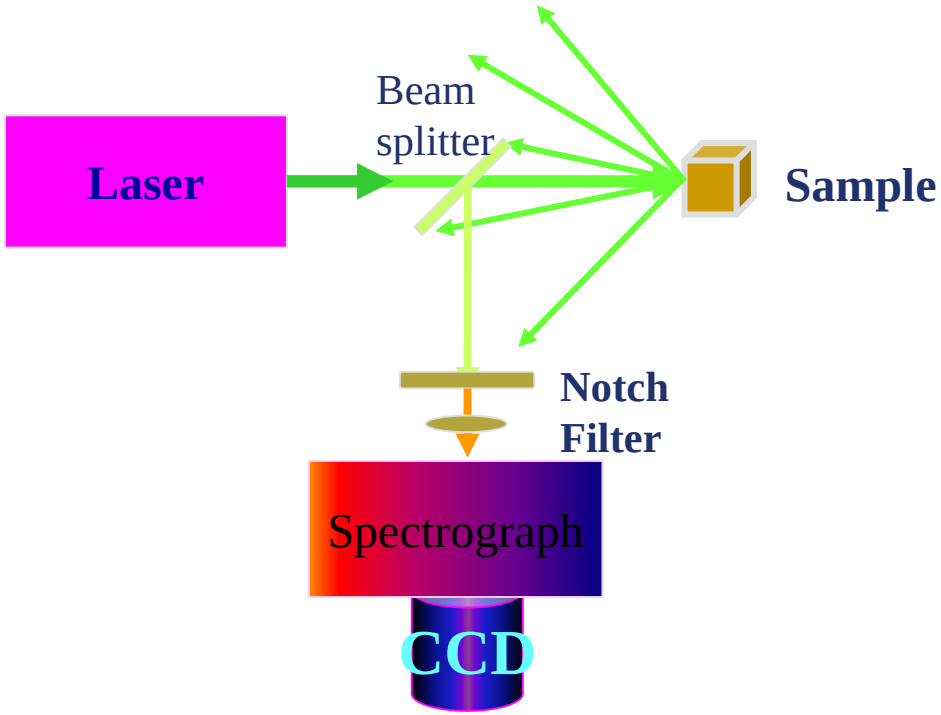
- **5” system (532 nm) (fiber optic coupled)**
- **5” system (532 nm) (direct coupled)**
- **8” system (532 nm)**
- **8” UV system (248 nm)**
- **16” UV system (248 nm)**
- **8” Raman+LIBS system**
- **8” Raman (785 nm)**
- **2” system (532 nm)**
- **3.5” system (tunable UV)**
- **2.5” Raman+LIBS+LINF+LIDAR (532 nm)**
- **12” UV system (248 nm, 266 nm)**





What is Raman spectroscopy?
Why need Raman spectra?

Prof. Sir C. V. Raman
Nobel Prize 1930



Raman spectra

↓

Vibrational modes of molecules

$$\omega = \sqrt{\frac{k}{\mu}}$$

↓

Depends on atomic mass, bond lengths, bond strength, configuration, etc…

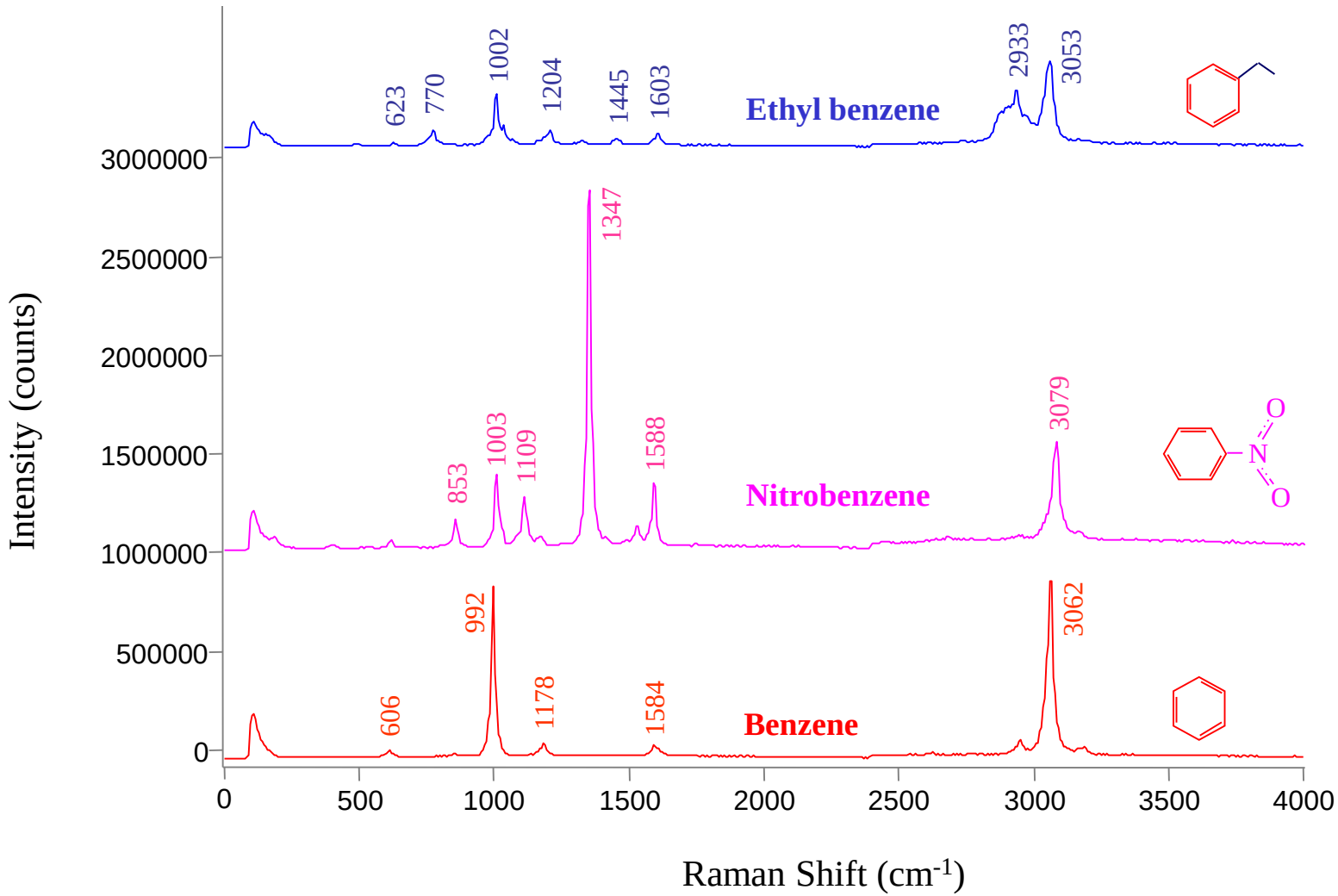
↓

Unique spectrum for each molecule

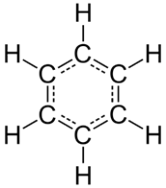
*** Raman Fingerprints: Chemical detection with very high confidence level**

Example of Raman Spectra:

- **Raman spectroscopy can distinguish between very similar chemicals**



$$\omega = \sqrt{\frac{k}{\mu}}$$



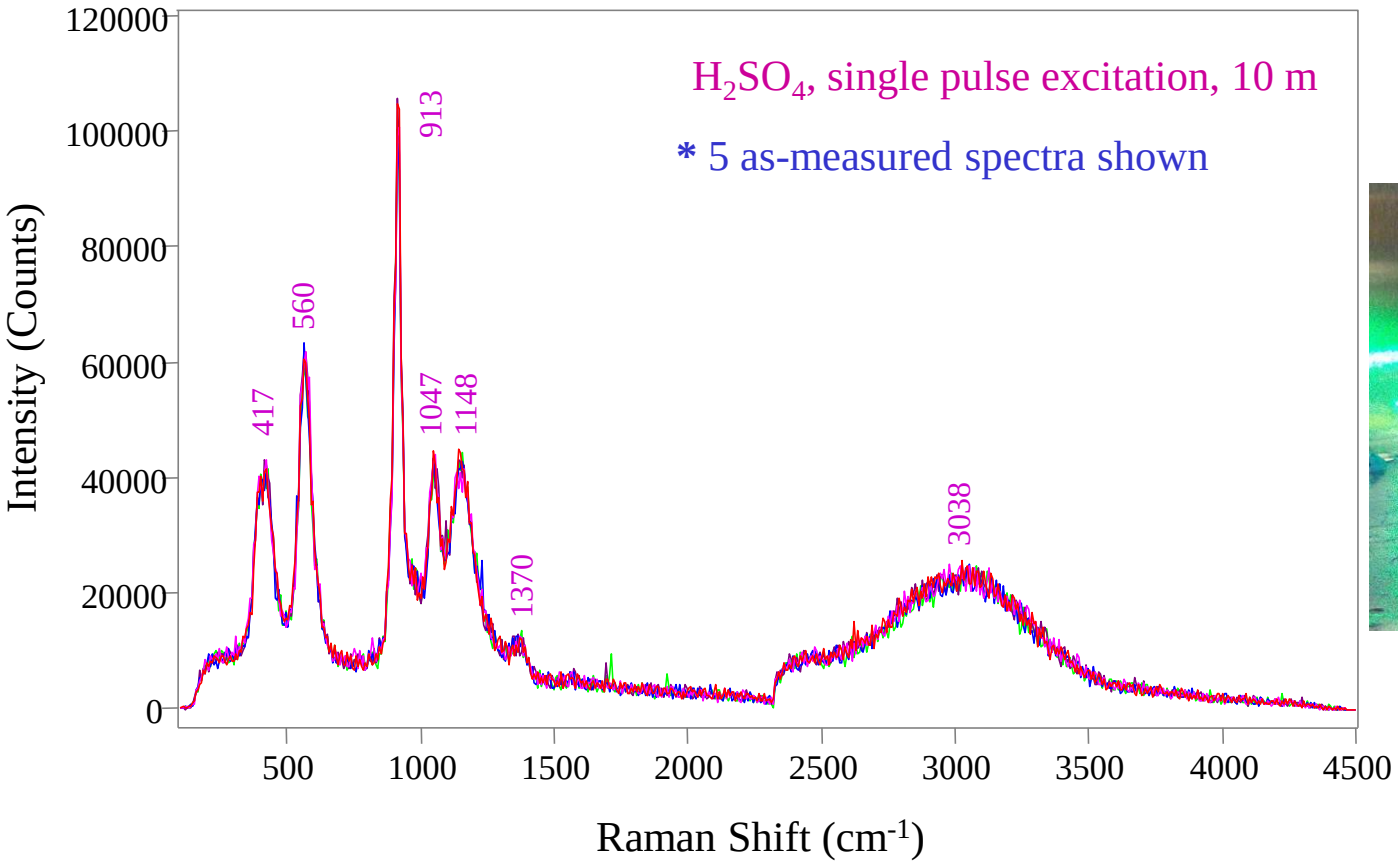
$$c = f\,\lambda$$

Always the same unique spectrum for a chemical !!!

* Good technique for detecting chemicals you don't want to handle.
* No sample preparation

(Chemical waste sites, airport)

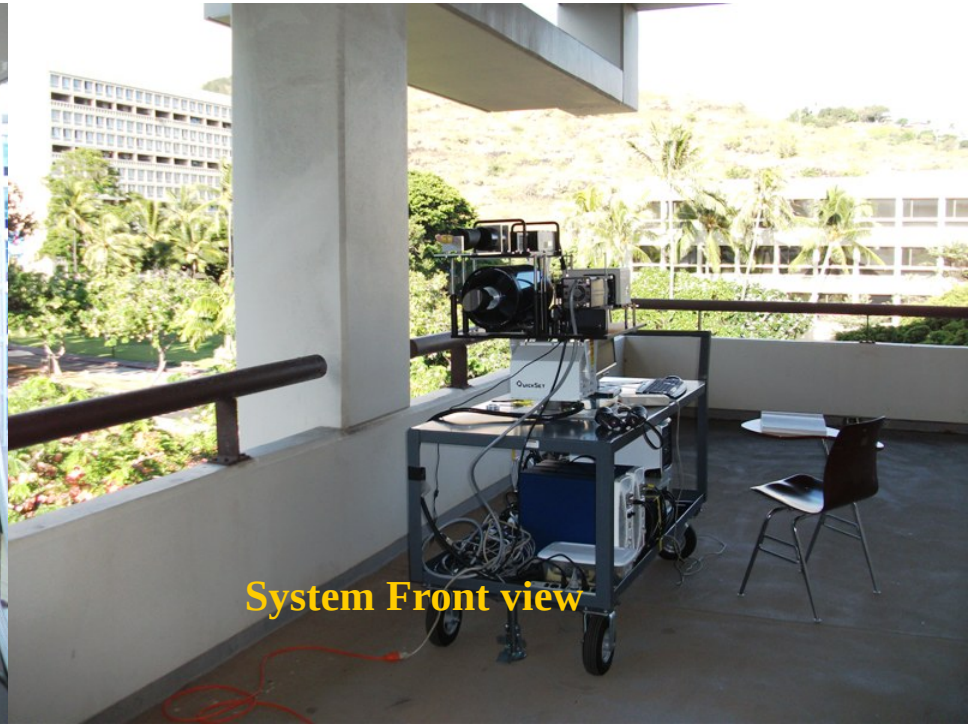
Single pulse Raman detection of **Conc. Sulfuric Acid** from 10 m



55 mJ/pulse, gate width 100 ns, slit 50 µm

Single Pulse Raman from 120 m

Detection time = 100 ns



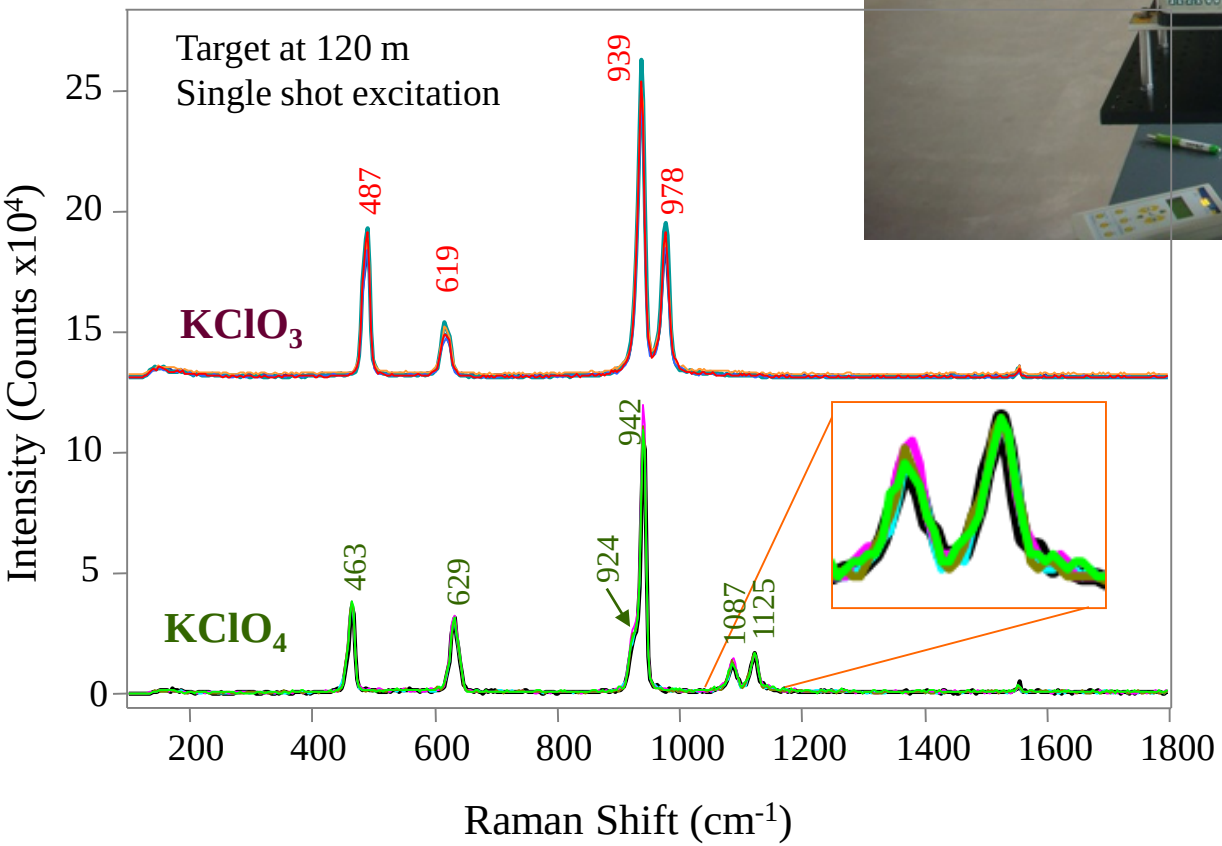
Integrated Remote Raman+LIBS System

Key Components:

(a) Dual Pulse Laser, 532 nm, 15 Hz, 100 mJ/pulse
(b) One gated intensified detector (ICCD)
(c) One high resolution, high throughput spectrograph
(d) 8-inch Telescope

Single shot Raman detection of Potassium chlorate & Potassium perchlorate at 120 m

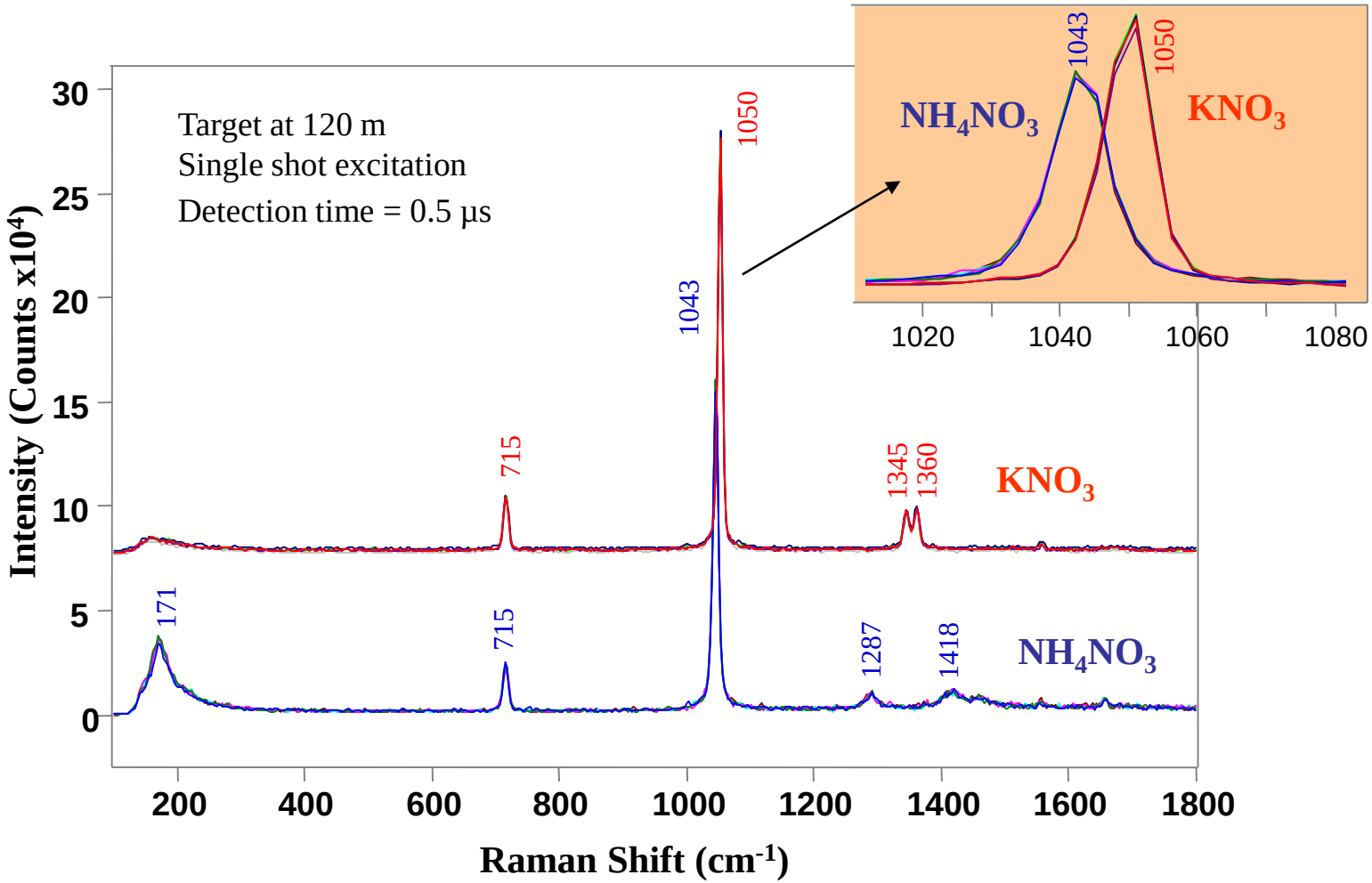
* **Good reproducibility**
  (showing 5 spectra as measured)
* Good quality (High S/N)



100 mJ, 532 nm, 50 µm slit,
laser spot size 1 cm (diameter).

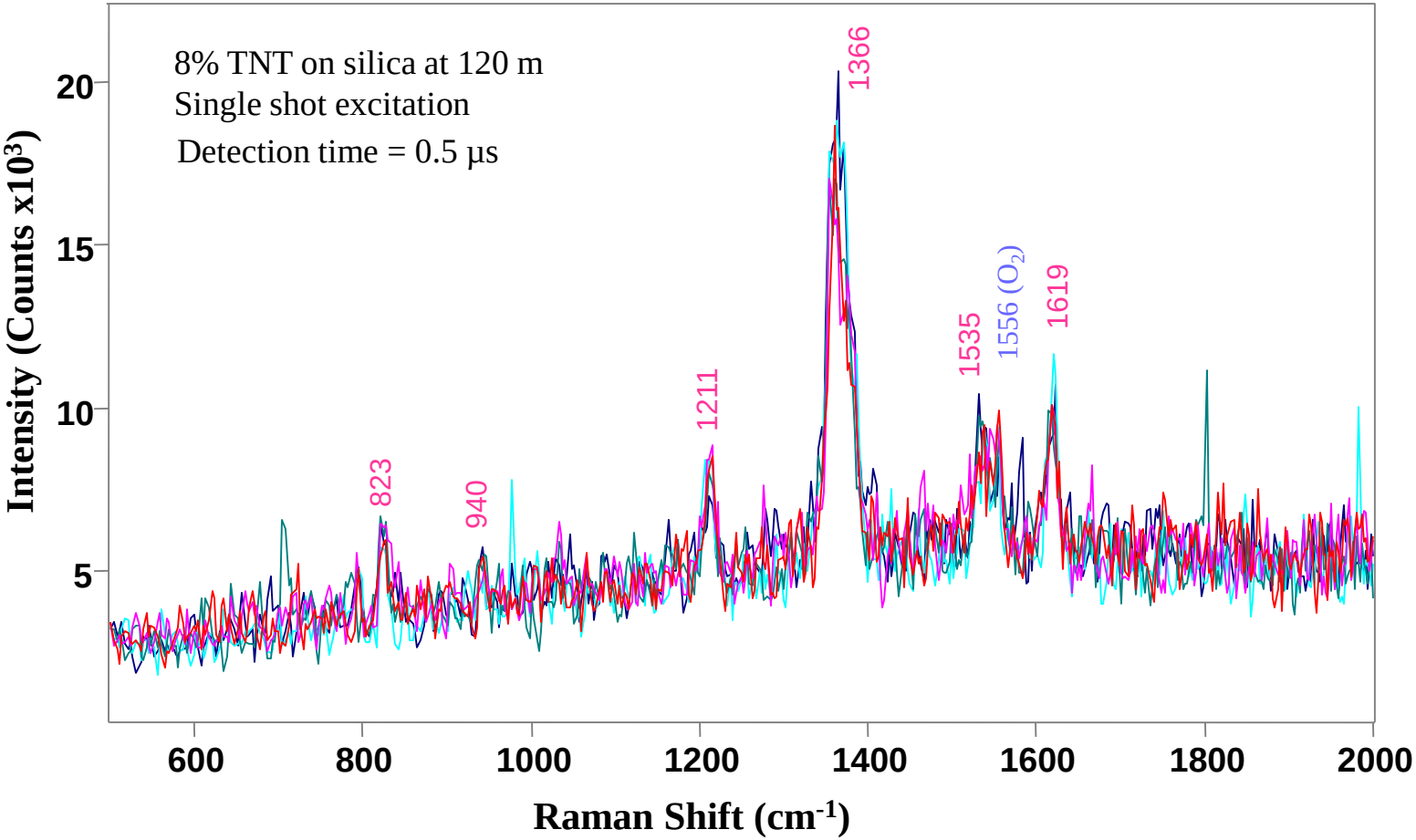
Single shot Raman detection of Ammonium Nitrate & Potassium Nitrate at 120 m distance through sealed glass bottles

*** Good reproducibility** (showing 5 measurements- as measured)



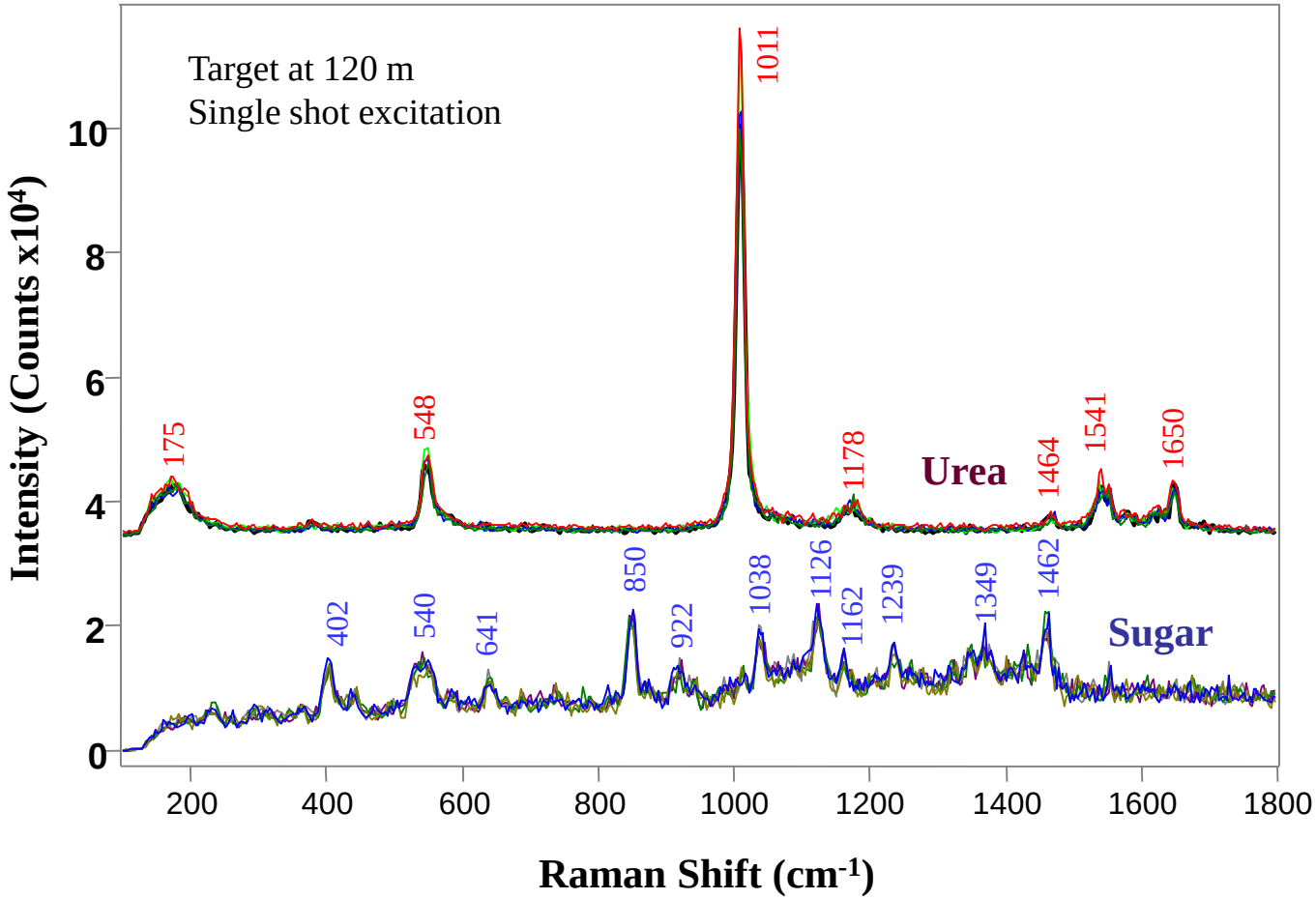
Single shot detection of 8% TNT on silica (NESTT sample) at 120 m distance

*** Good reproducibility** (showing 5 measurements- as measured)



Single shot Raman detection of Urea and Sugar at 120 m distance through sealed glass bottles

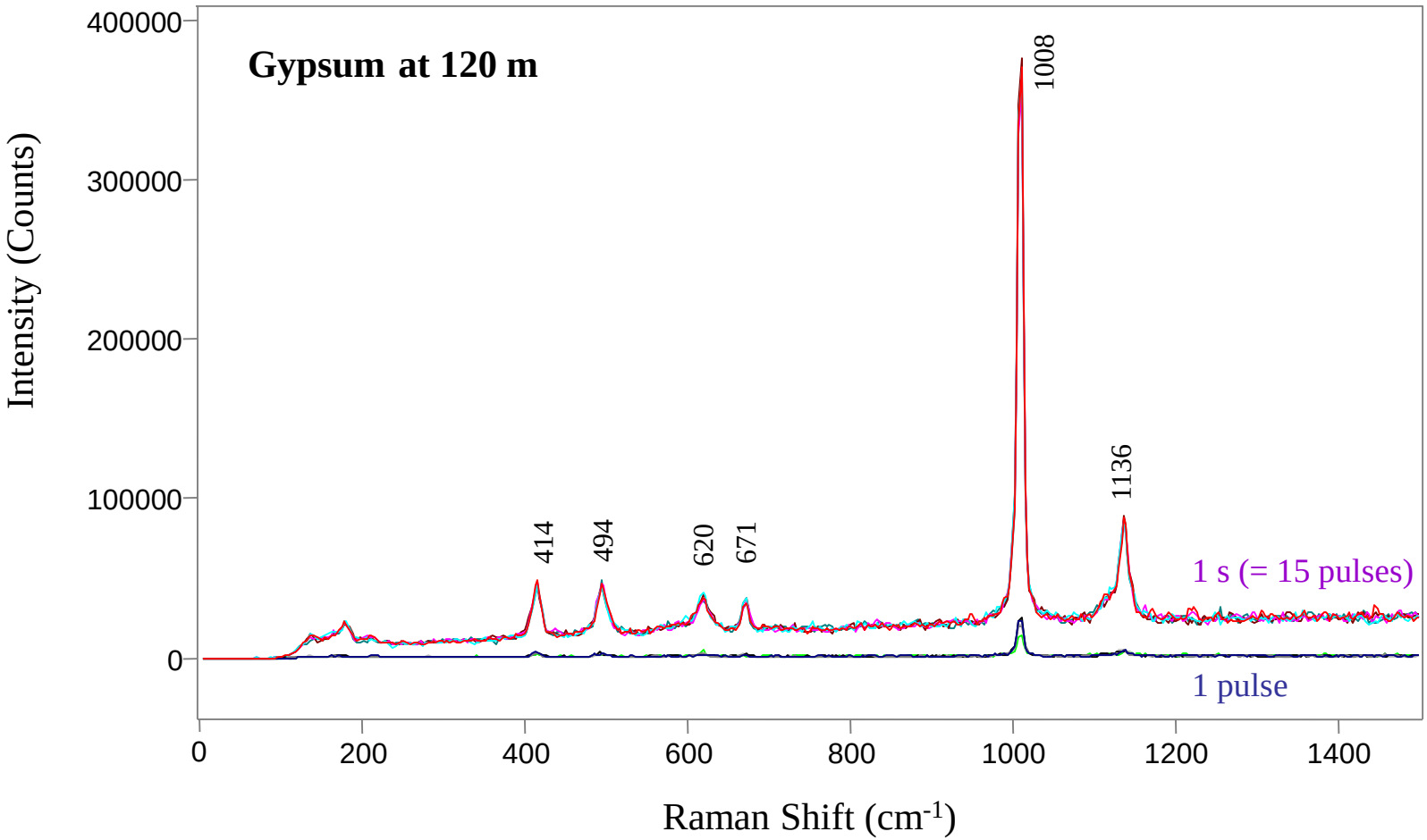
*** Good reproducibility** (showing 5 measurements- as measured)



100 mJ, 532 nm, 50 µm slit,
laser spot size 1 cm (diameter).

Significant improvement in Raman signal (1 s)

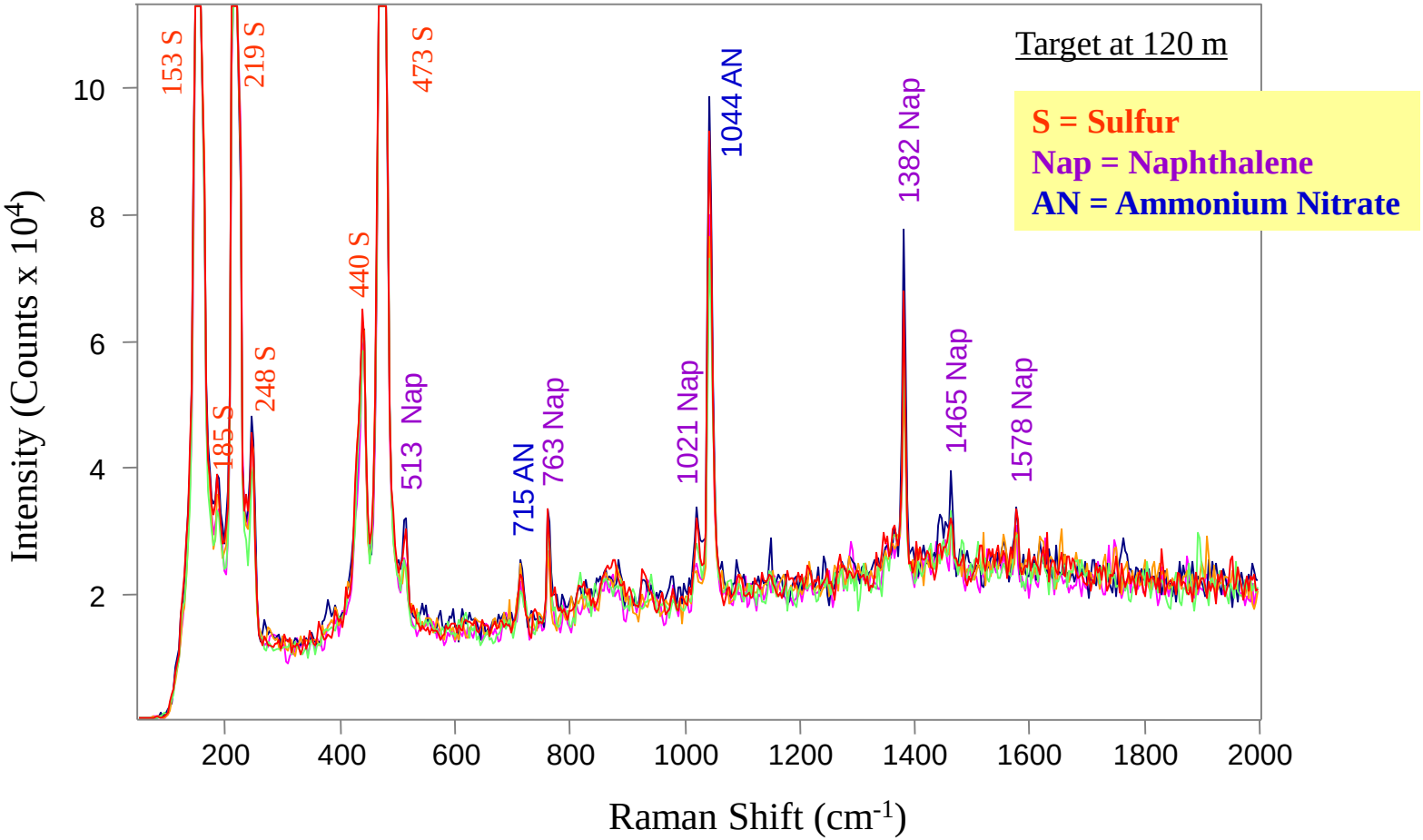
*** Good reproducibility** (5 measurements shown)



Raman Detection of Mixed grains of chemicals at 120 m distance

*** 1 s detection time**

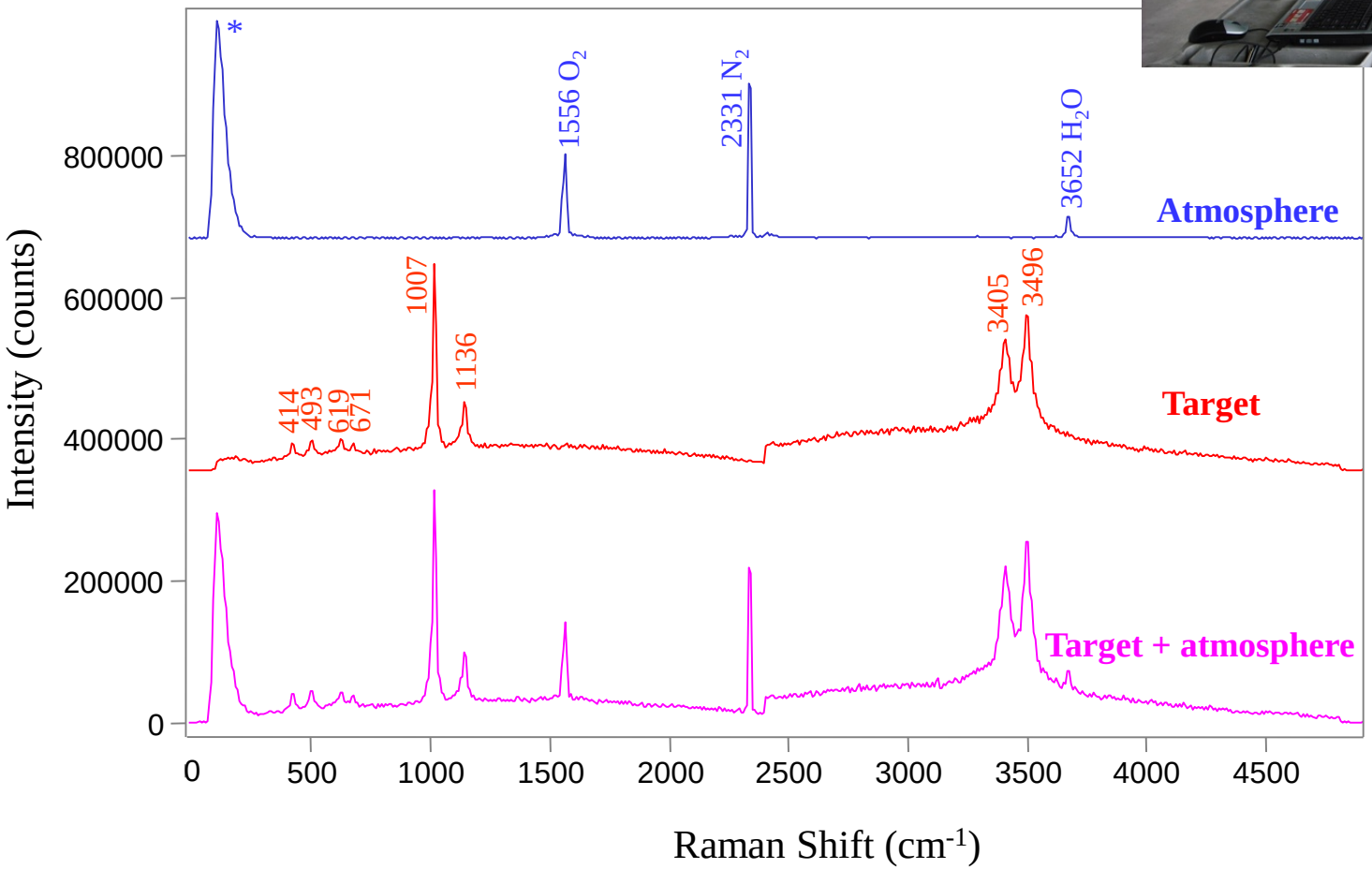
*** Good reproducibility** (5 measurements shown)



100 mJ/pulse, 15 Hz, 532 nm, 50 micron slit, laser spot size 1 cm.

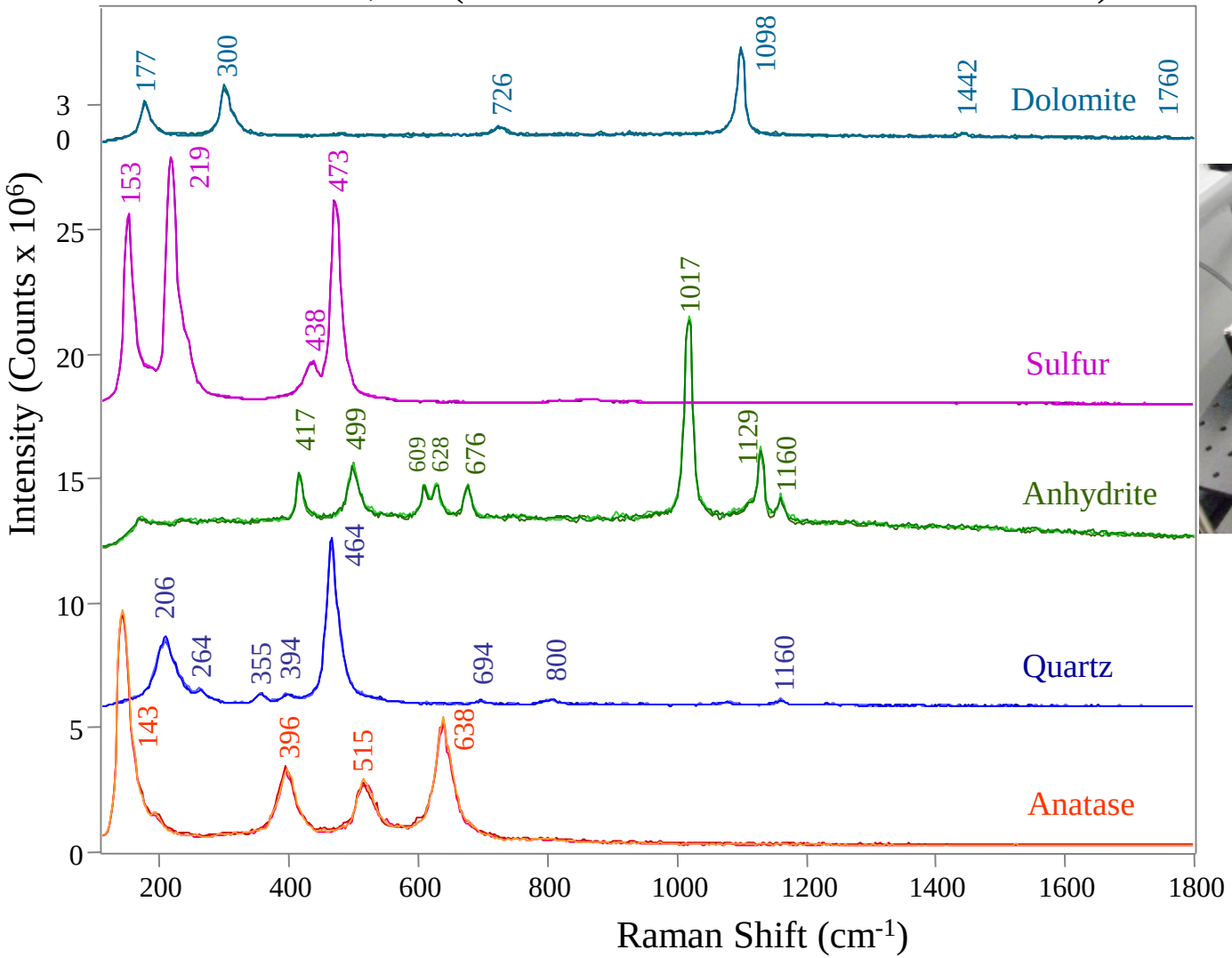
• **Detection of atmosphere, target mineral and both (as measured spectra)**

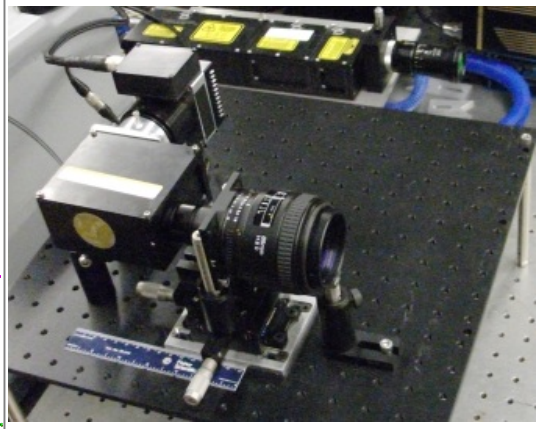
Target (Gypsum $CaSO_4.2H_2O$) at 50 m



2” compact Raman+LIBS system

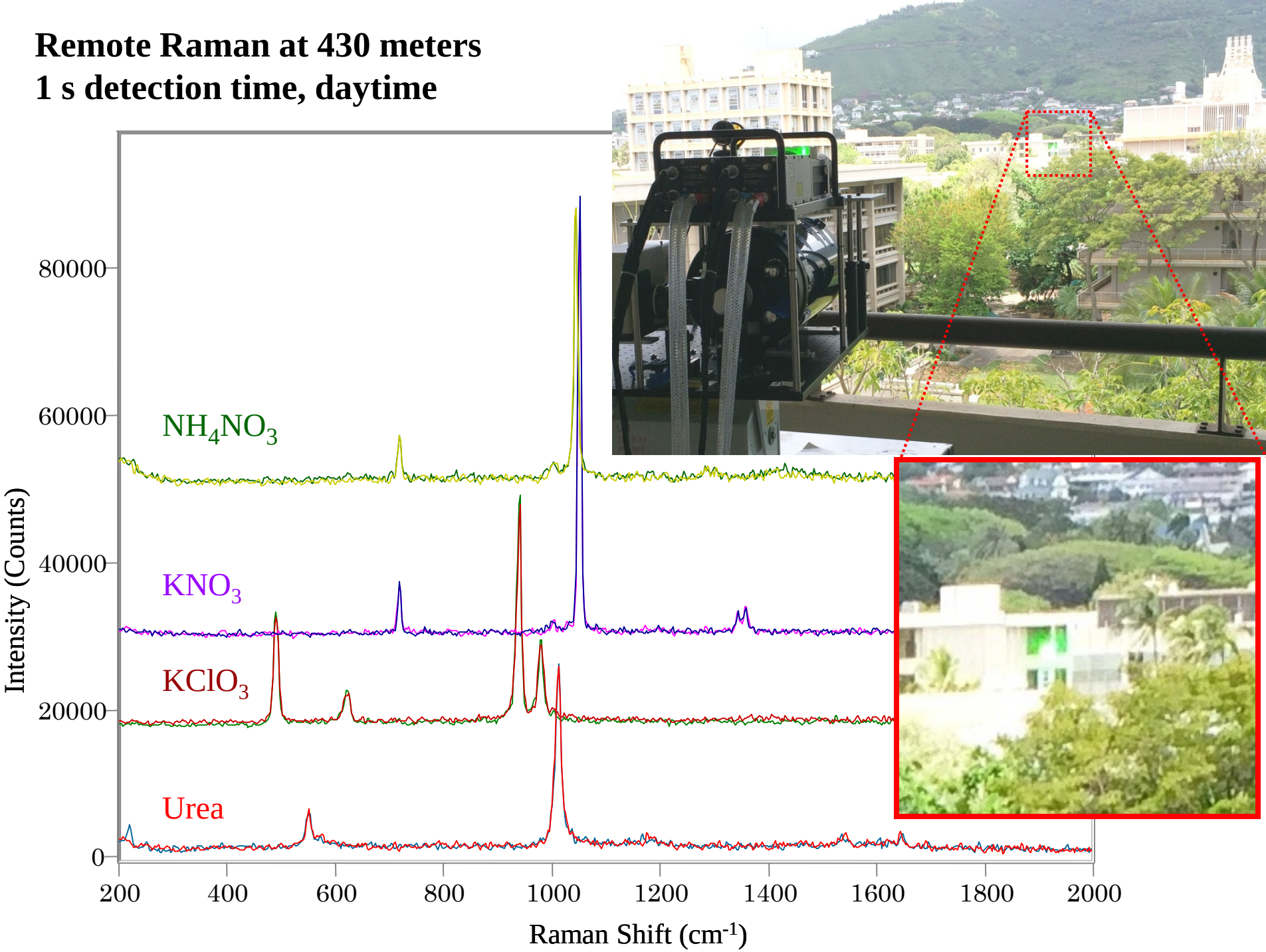
Minerals at 9 m, 1 s (**3 measurements shown** for each mineral)





532 nm, 30 mJ/pulse

Remote Raman at 430 meters
1 s detection time, daytime



Standoff Raman (532 nm) detection through sealed containers

A	B	C	D	E
T= 81%	54%	18%	5.6%	1.7%

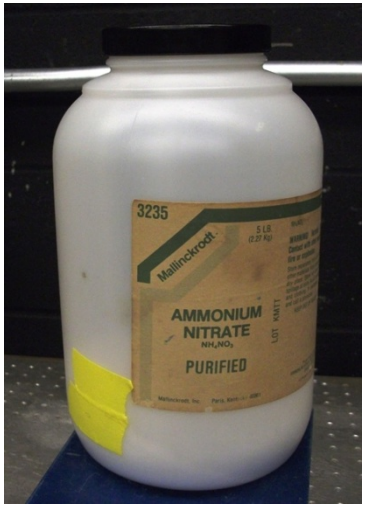
A: borosilicate glass vial (20 ml)

B: polypropylene (PP) vial (30 ml)

C: high-density polyethylene (HDPE) bottle (60 ml)

D: amber glass bottle (75 ml)

E: dark brown glass bottle (500 ml)



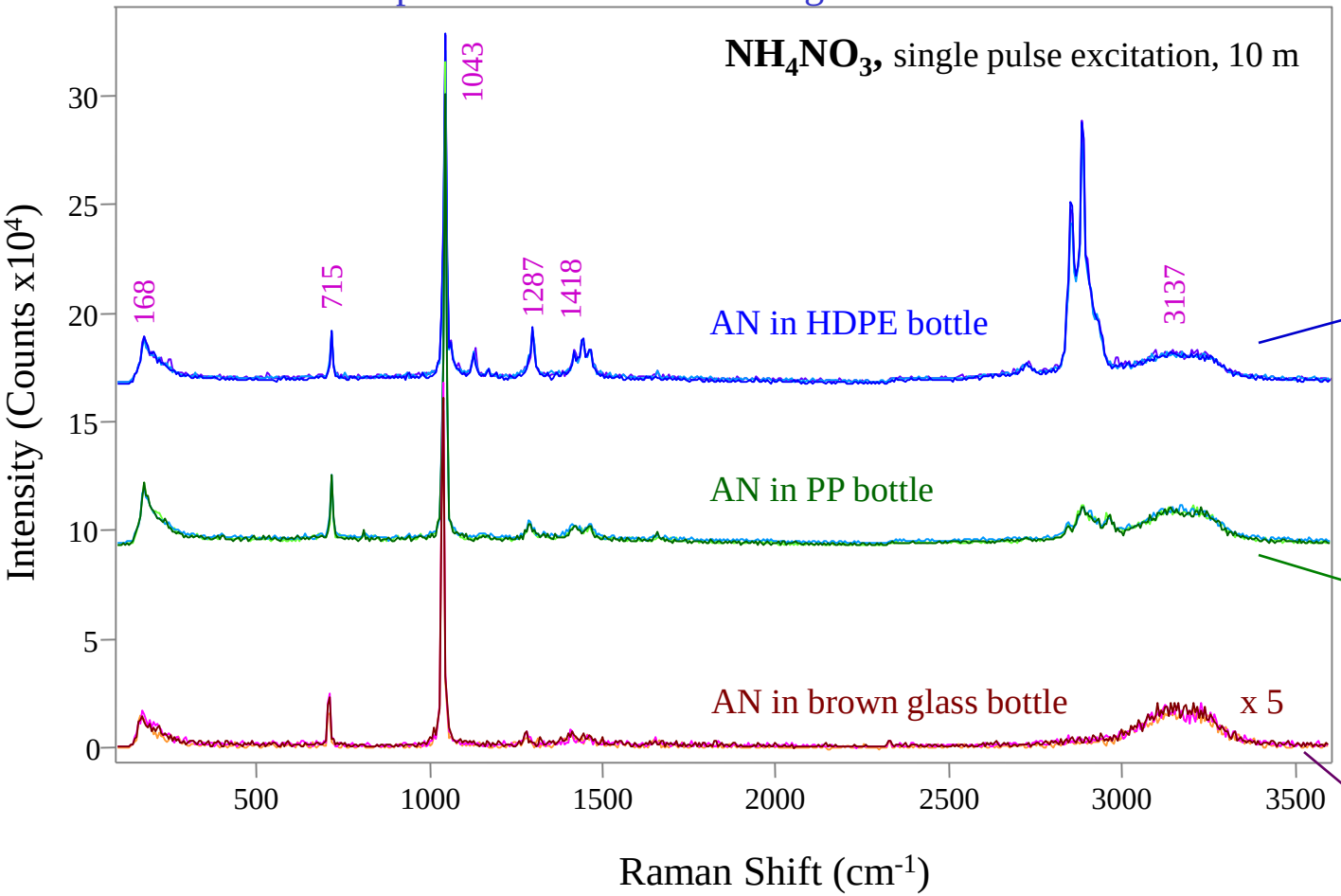
HDPE

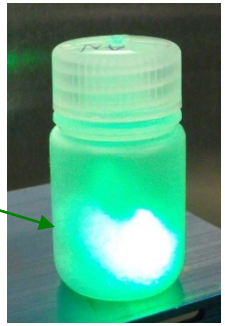
Water bottle

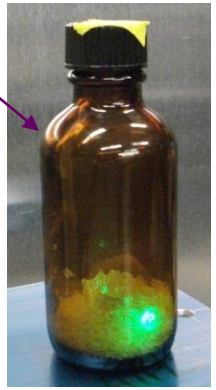
Bubble wraps containing 20 ml glass vials

Single pulse Raman detection of Ammonium Nitrate at 10 m distance through sealed bottles

* 3 as measured spectra shown for each target



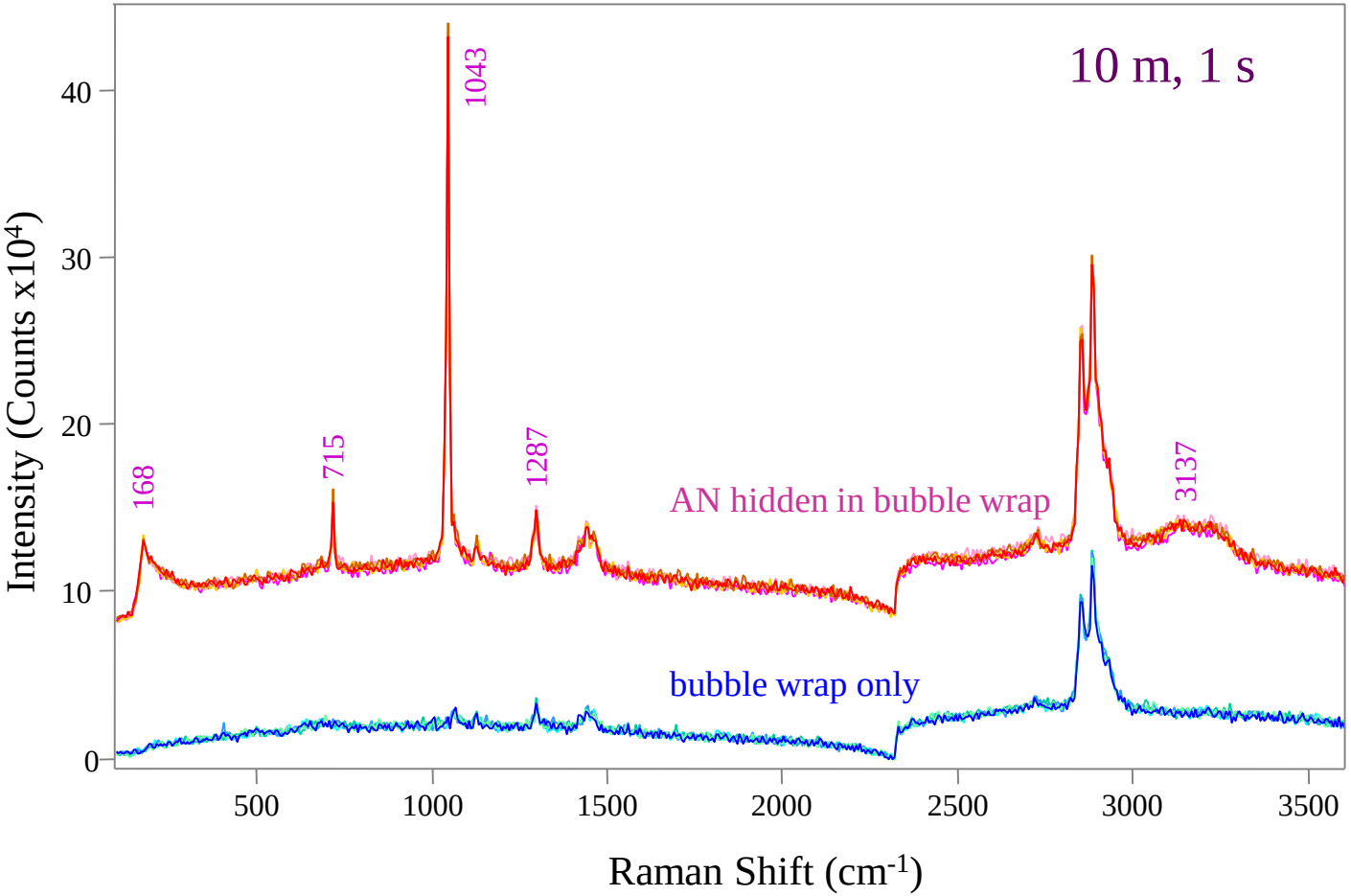




532 nm, 55 mJ/pulse, gate width 100 ns, slit 50 µm

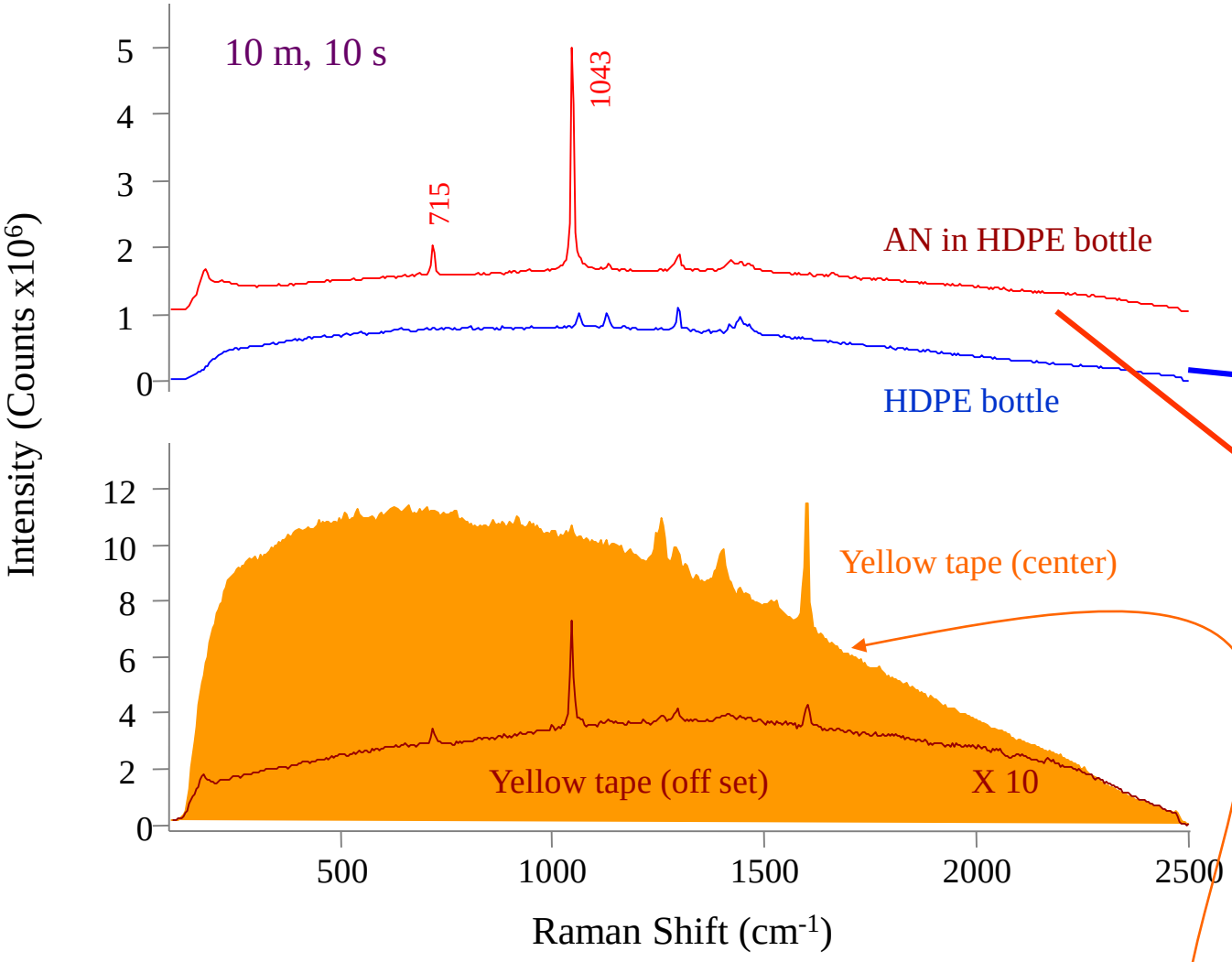
Raman detection of hidden glass vial of Ammonium Nitrate through plastic bubble wrap

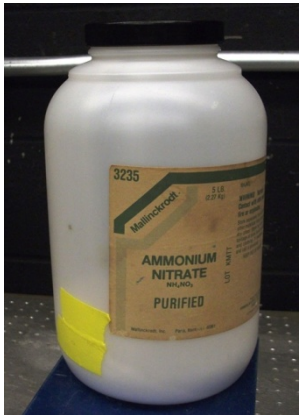
* 5 as-measured spectra shown



532 nm, 55 mJ/pulse, 15 hz, gate width 100 ns, slit 50 µm

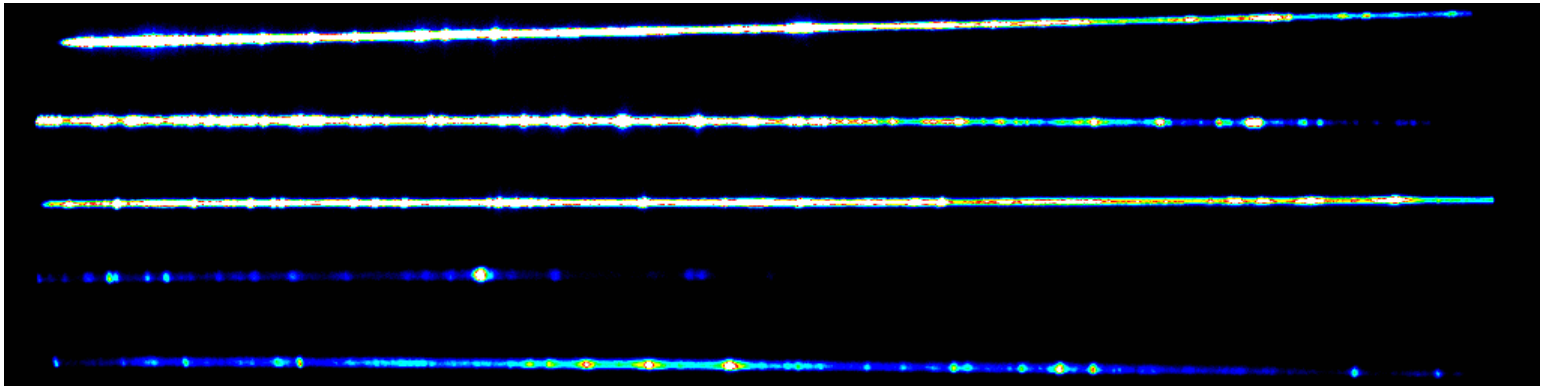
Raman detection of AN through fluorescent label on HDPE bottle





Raman+LIBS Spectrograph with 5 spectral images on one ICCD detector

ICCD Image (1024 x 256 pixels)



Wavelength Range

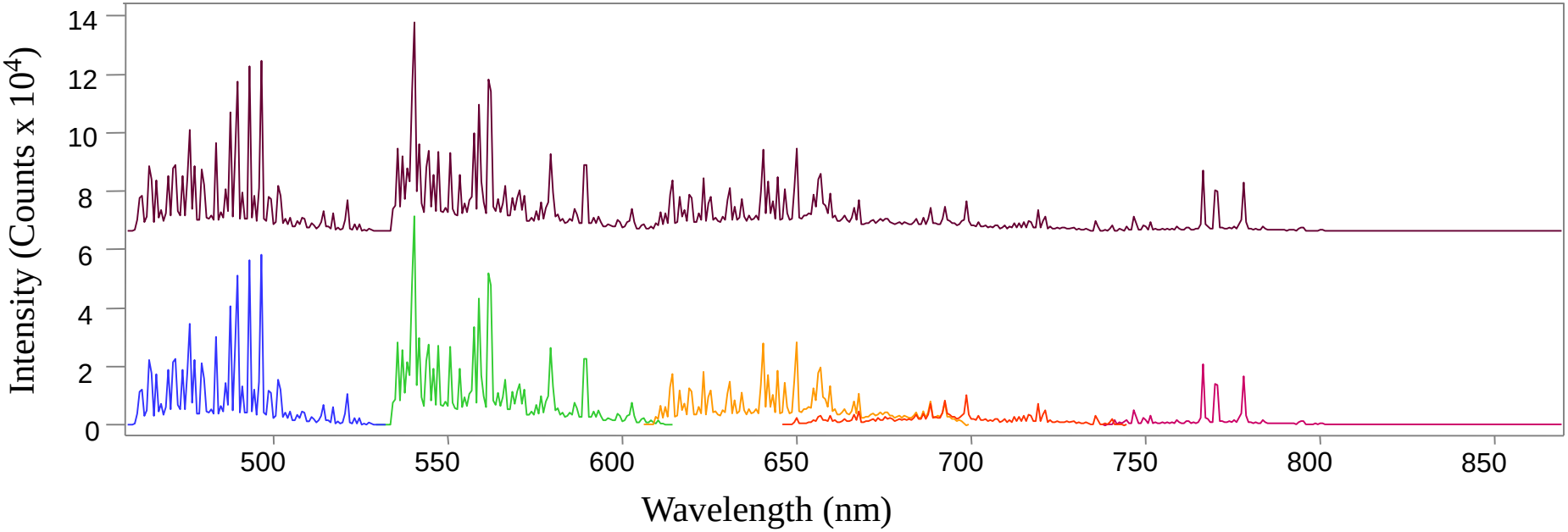
532.5 – 612.7 nm

457.3 – 530.9 nm

604.1 – 697.9 nm

736.5 – 869.4 nm

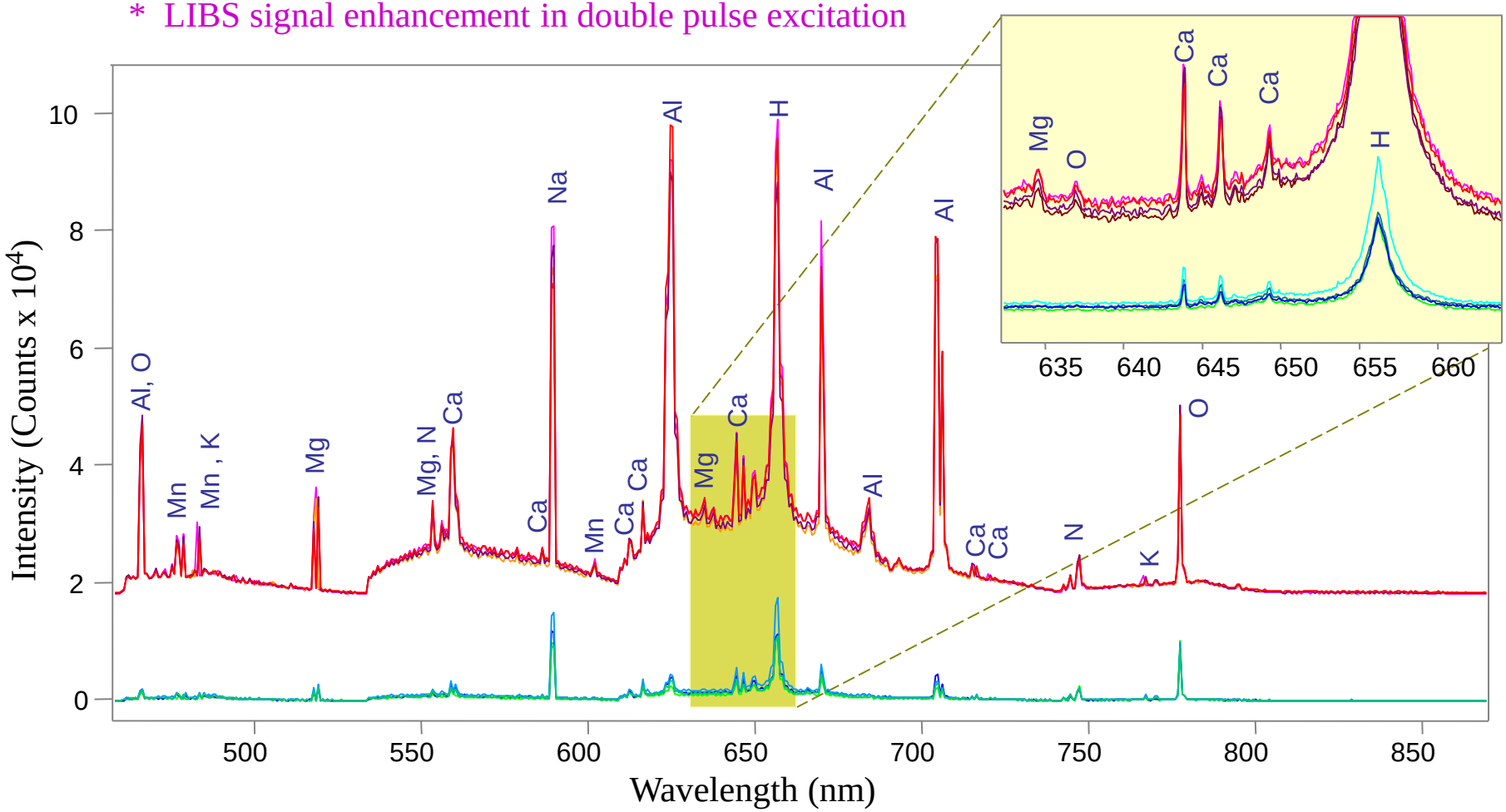
645.2 – 745.7 nm



Steel, at 9 m, 1 double pulse LIBS, Pulse separation 1 µs, 100 mJ/pulse, gate delay 1 µs, gate width 4 µs. ICCD Gain 25

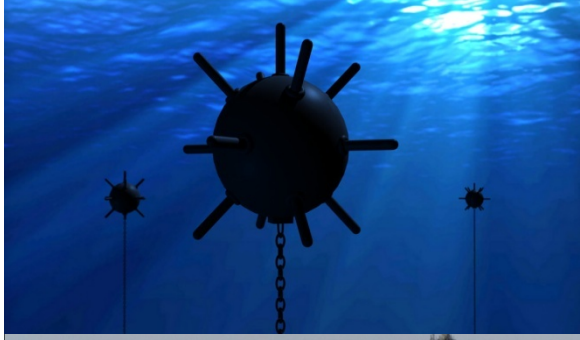
Single pulse and double pulse LIBS spectra of Aluminum sheet at 9 m.

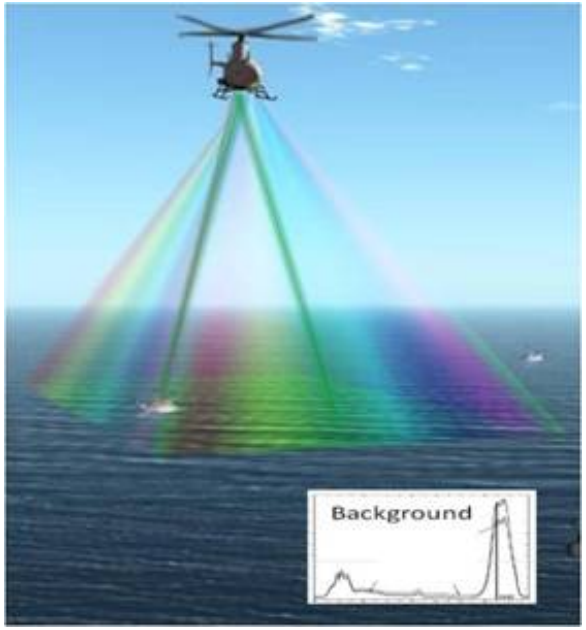
* Spectra showing good reproducibility (4 measurements shown)
* LIBS signal enhancement in double pulse excitation



Gate delay 1 µs, Gate width 20 µs, ICCD gain 10%, Double pulse separation 1 µs, 100 mJ/pulse, spot size 1 mm (dia)
There are small shot to shot variations.

Raman and Fluorescence Imaging LIDAR (RFI-LIDAR) for sea mine detection





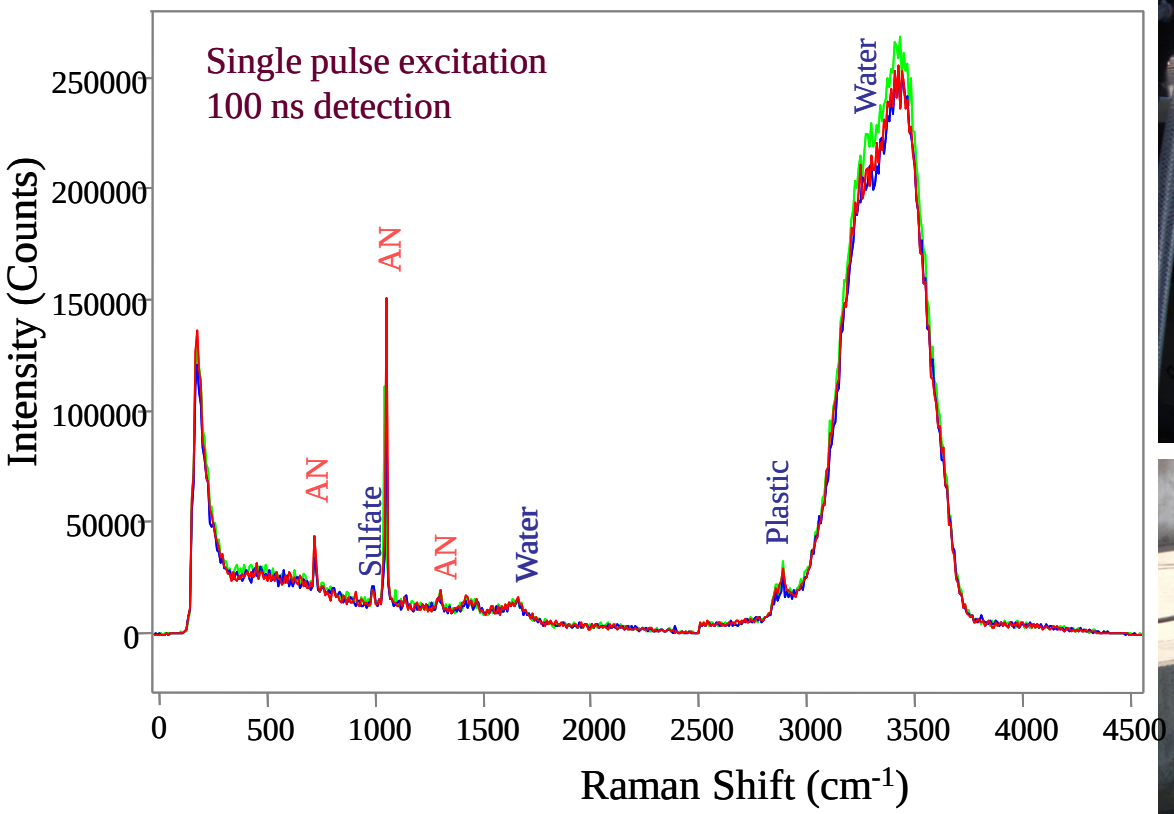
Ocean LIDAR (532 nm)

Issues:

* **No detection in the top 1-2 m surface layer**
* **Glint problem**
* **Signal from fishes, plants, air bubbles…**

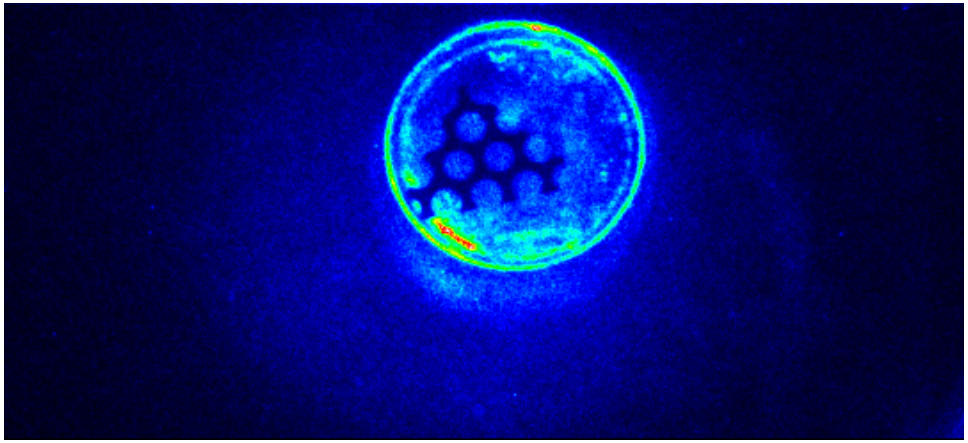
Single Shot Detection of AN inside HDPE plastic bottle at 2 m Seawater Depth with 532 nm Laser

*3 as-measured spectra shown



* Can detect explosives in plastic bags underwater
* Metals have no Raman signal

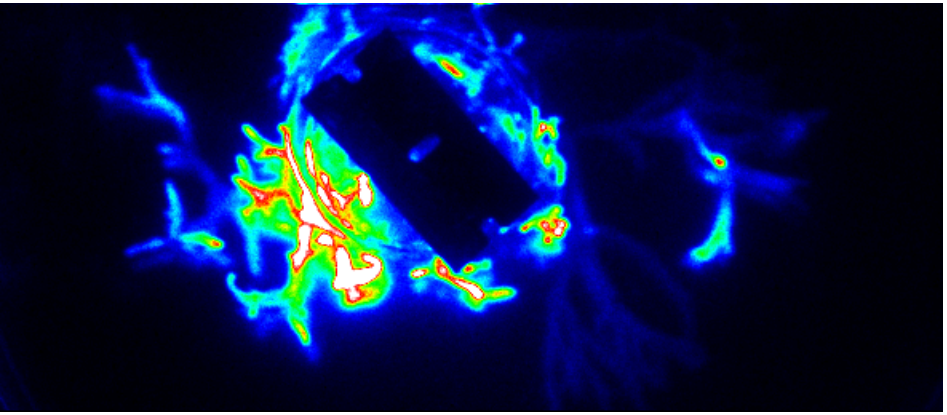
Detection of both opaque metal object and also the transparent plastic dish using the image contrast.



Raman Image

Single pulse detection,
detection time **300 ns**

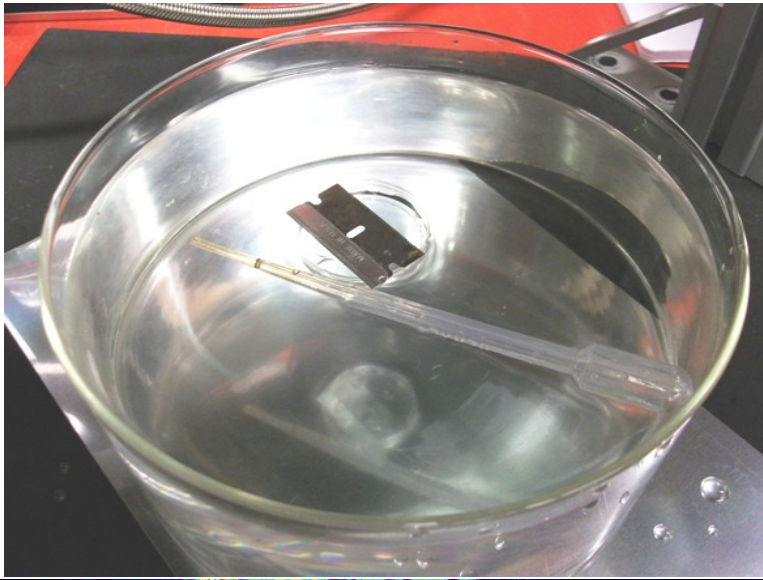
Detection in presence of bio-fluorescence

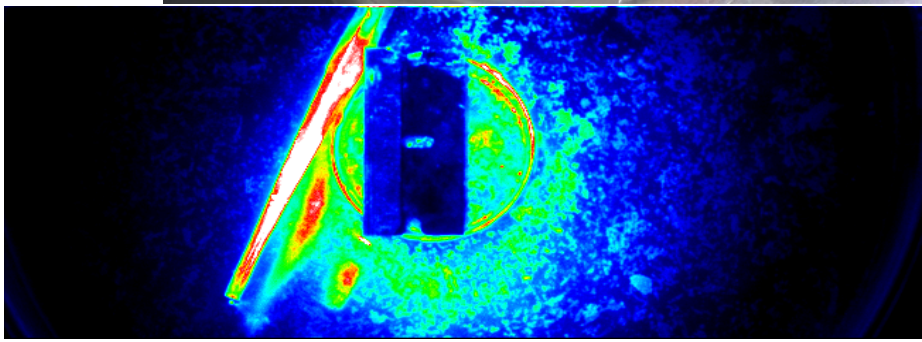


Detection of oil spill

One drop (0.1 ml) of crude oil in 2000 ml of water (50 ppm)

•Oil film is few micron thick





Current projects:

1. NASA Mars2020 mission: Los Alamos National Lab
   SuperCam Instrument

2. NASA EPSCoR: Standoff biofinder+Chemical analyzer

3. NASA PICASSO: Standoff Raman Line Scanner

4. NASA STTR: Q Peak Inc. : Small laser for remote Raman+LIBS (phase I)

5. ONR: Underwater Raman system

6. ONR (code 30): Long range (~km) Raman system (low cost drone)

Thank you.