

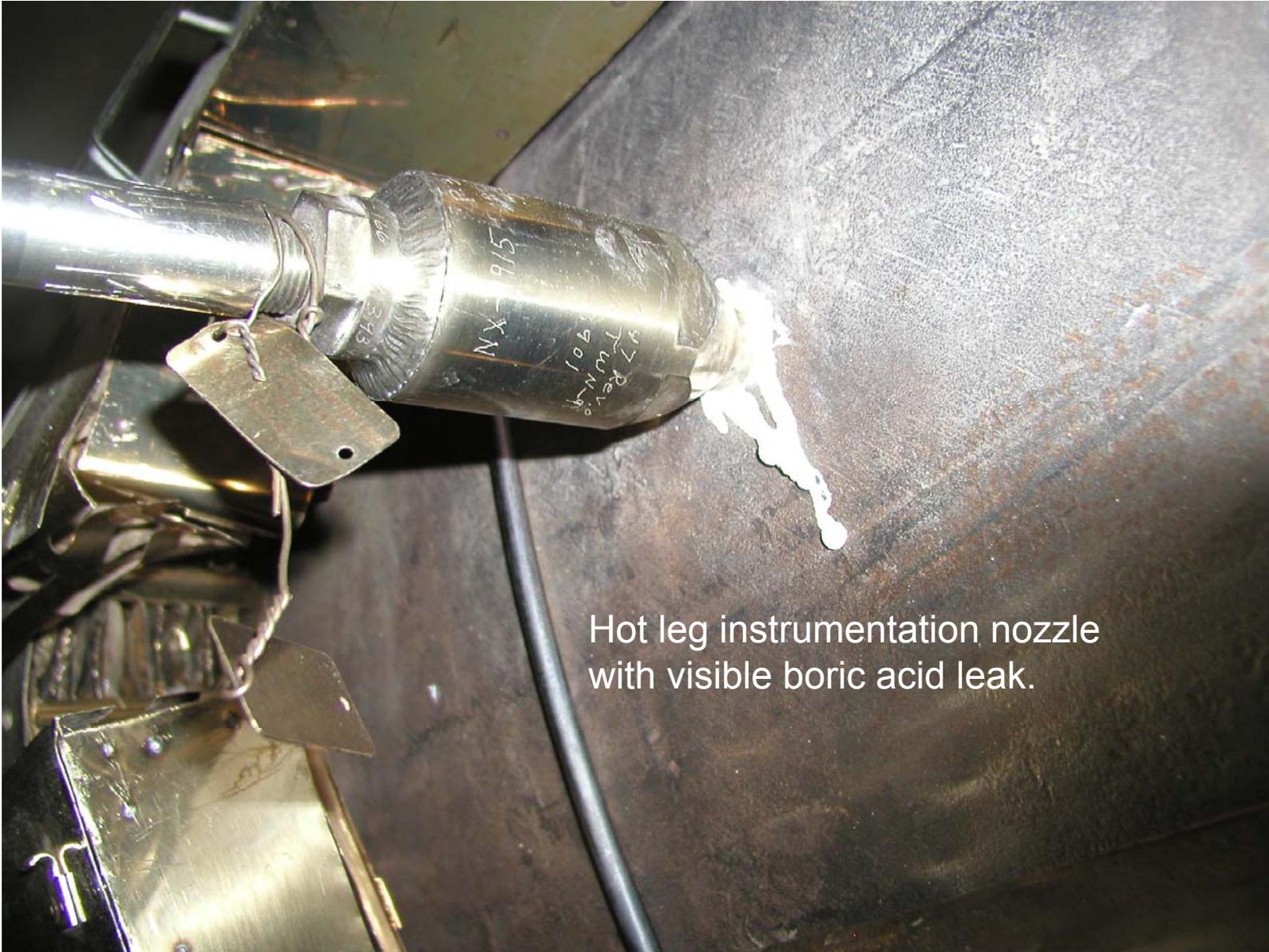
A Portable Remote Chemical Analyzer for Determination of the Composition of Deposits in Nuclear Power Plants

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Introduction

- A large electricity producer identified a need for a field test to determine unequivocally if an unidentified deposit is boric acid. (RCS). Other power plants requested a test for discriminating secondary coolant leaks from primary coolant leaks.
- Currently, pressure boundary leakage as a source of RCS deposits is identified visually, with confirmation using laboratory radiometric techniques.
- Radiometric techniques do not determine boric acid directly, and are subject to false positives and require interpretation.
- Symphotic TII have developed a technique for *in-situ* analysis that gives positive identification of boric acid deposits without sample removal.



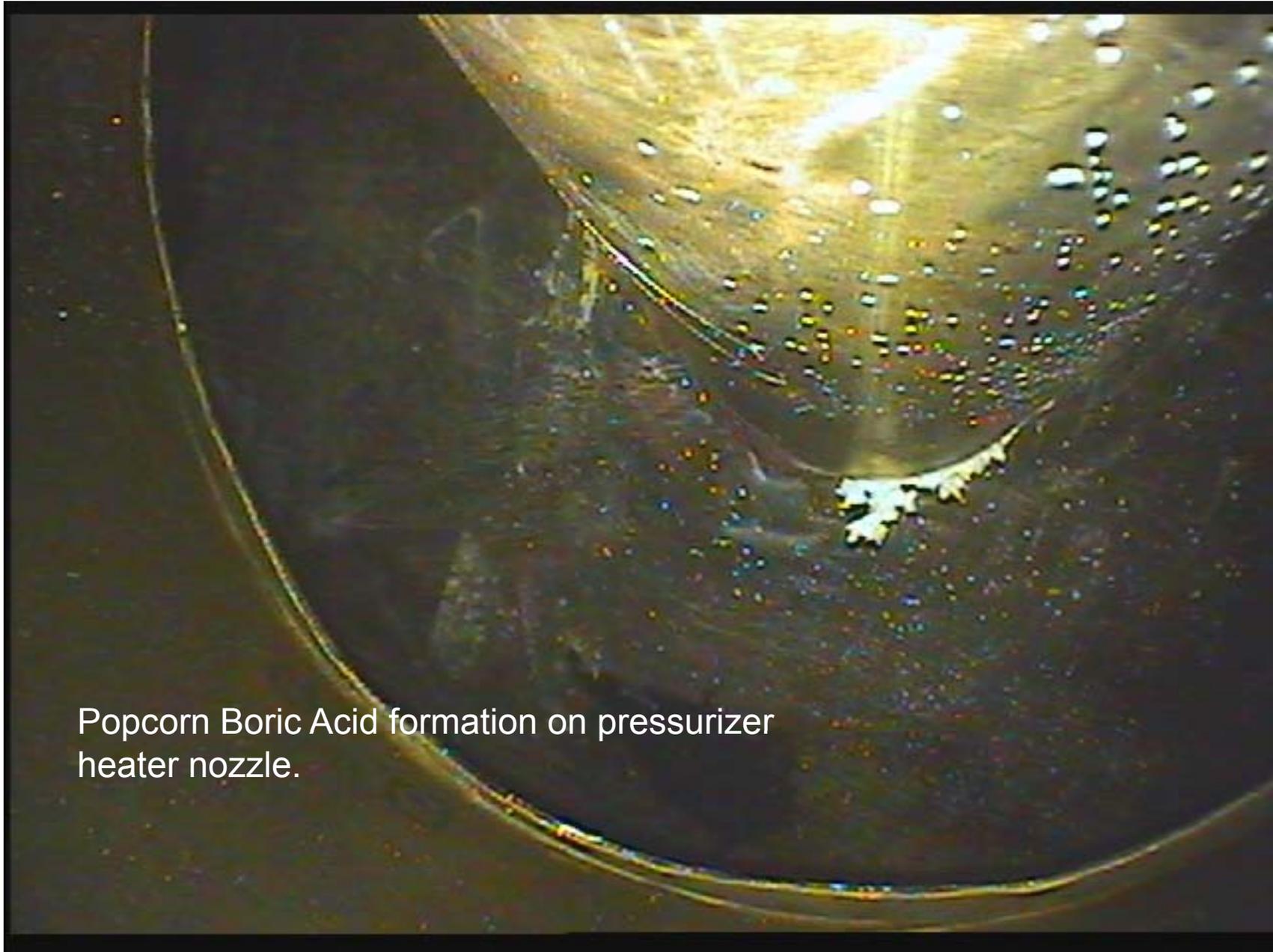
Hot leg instrumentation nozzle
with visible boric acid leak.



Reactor vessel,
bottom mounted
instrumentation
nozzle

04/12/2003

Courtesy of South Texas Project



Popcorn Boric Acid formation on pressurizer heater nozzle.

Spraylat and
white paint
on BMI
penetrations
(NOT Boric
acid)





Tape residue

Problems with current techniques

- Cross contamination can cause false positives
- False positives may result in unnecessary repairs and excess radiation exposure.
- Other contamination (spills, maintenance activities, etc.) may give false radiometric results.
- Sampling is required—locations may be inaccessible or deposits too small

In-situ analysis using spectroscopy

- We have developed instrumentation for in situ analysis using the InSITEtm spectroscopy system—a Raman spectrograph with a remote probe.
- Raman spectroscopy allows clear identification of boric acid.
- Raman can also identify Sodium Molybdate deposits

What is Raman Spectroscopy?

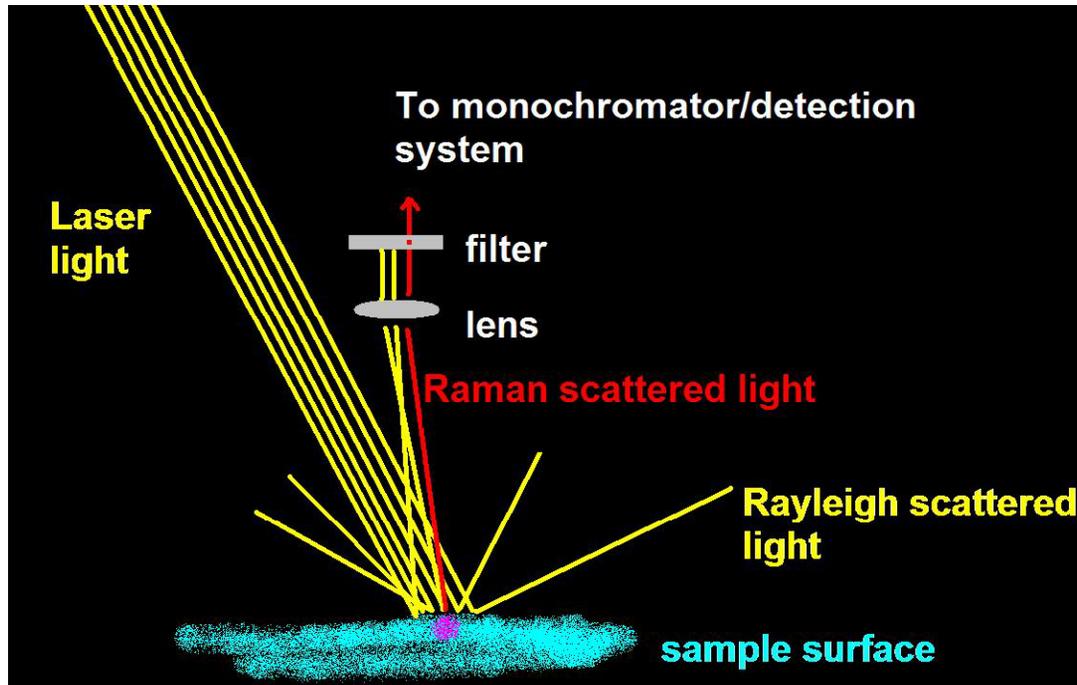
- Sir C.V. Raman was awarded the Nobel price for Physics in 1930 for his discovery of the Raman phenomena, but it was not until the recent development of high quality lasers as monochromatic light sources that Raman spectroscopy has become a routine analytical technique.



What is Raman Spectroscopy?

- Raman spectroscopy takes advantage of the inelastic scattering of monochromatic light by molecules. During this process energy is exchanged between photons and molecules: the scattered photons may be of higher or lower energy than the incident photons. The difference in energy is made up by a change in the vibrational energy of the molecules.
- Each substance has a characteristic Raman spectral “fingerprint” or “signature”.

Raman Concept



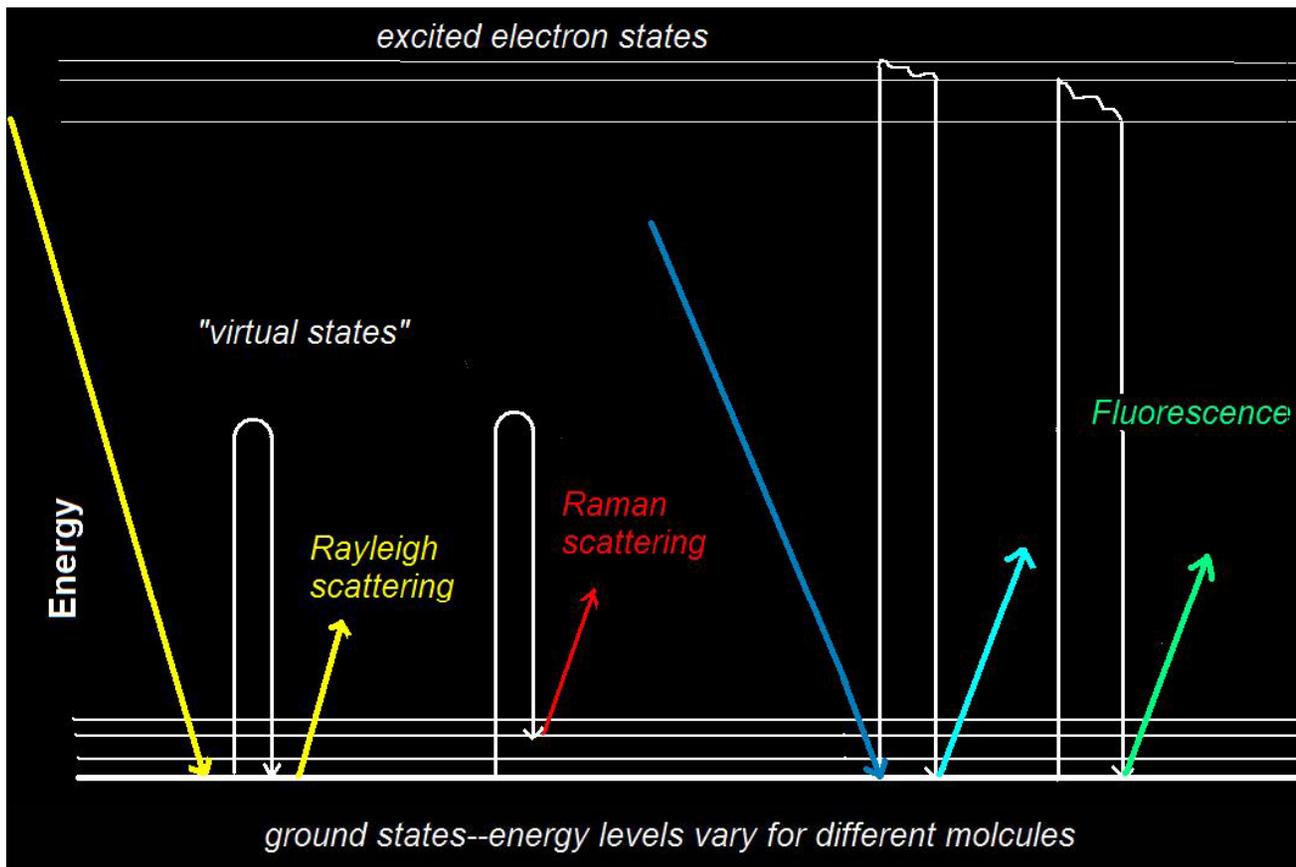
- Laser light strikes the sample and is scattered at the surface of the sample

- The energy of the laser causes an distortion of the electron distribution in the covalent bonds of the molecules on the surface (excitation to “virtual states”)

- The molecule’s distorted electron distribution returns to its ground state and the light is given off at the same frequency as the laser light, but in random directions (Rayleigh scattering)

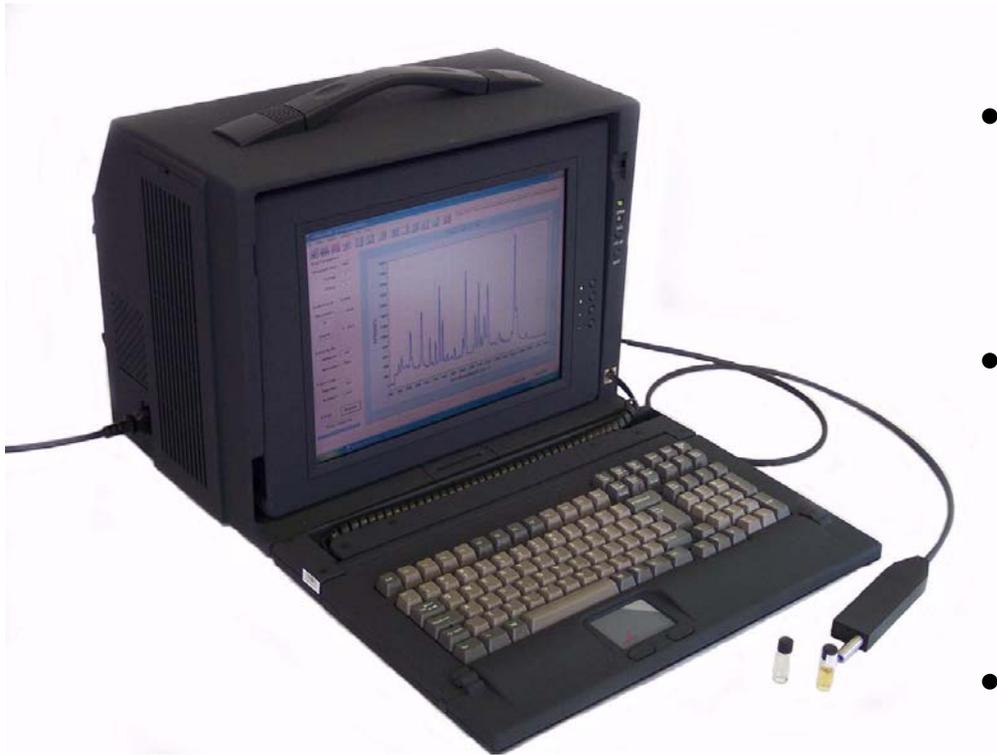
- A small amount of the molecules lose energy to an elevated energy level, higher than the lowest ground state, and the light is given off at a lower frequency (less energy). This amounts to only 1 part in 10 million of the scattered light. The amount of frequency shift depends on the molecular structure, but not on the laser wavelength.

Rayleigh scattering, Raman scattering and Fluorescence



- If there are excited electronic states low enough, or if the laser energy is high enough, fluorescence can also occur. This generally interferes with Raman spectra

The InSITE™ Analyzer



Winner of the 2006 NEI Top Industry Practice Vendor Award

- Portable laser/spectrometer/data station
- Features high performance Divya™ frequency stabilized laser
- Remote probe that can be hand carried or poled into position
- Selection of probe tips for use in difficult locations.

The InSITE™ Analyzer



SPECIFICATIONS

- Fully Integrated Raman Analyzer with narrow linewidth, frequency stabilized laser, high resolution spectrograph, portable design.
- Excitation Source:
- Divya™ 785 nm or 808 nm, Frequency Stabilized, Narrow Linewidth Diode Laser Standard
- Laser Power: 150 to 200 mW or 300 to 400 mW
- Line width: 0.5 to 1 cm⁻¹
- Laser output: Fiber Coupled 100 μm fiber, 0.22 NA
- Laser Lifetime: >10,000 hours estimate
- Spectrometer Type: f/4 Crossed Czerny-Turner
- Resolution: <6 cm⁻¹
- Spectral Range: 200 cm⁻¹ to 2400 cm⁻¹
- CCD Linear Array Detector: Pixel Size : 14 μm x 200 μm (2048 Pixels)
- 12 Bit Digitization
- USB Interface or RS-232
- System Software
- Operating Environment: 10 – 40 °C

Sampling Head:

- Black Anodized Aluminum Probe
- Stainless Steel Probe Tip, Straight and right angle options
- Working Distance from Probe to Sample: 6 mm (0.3 NA) Standard, 3 mm (0.55 NA), 10 mm (0.3 NA) Optional
- Operating Environment: Up to 170 °F
- Fiber cable length: 100 ft

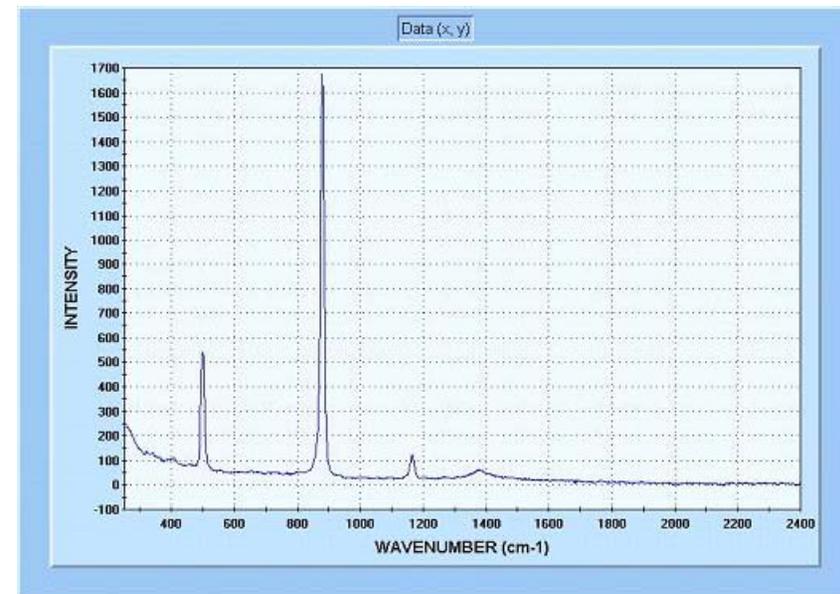


Sample of dried Boric Acid deposit on steel

Dried Boric Acid, H_3BO_3 ,
Natural Boric Acid is known as
sassolite.

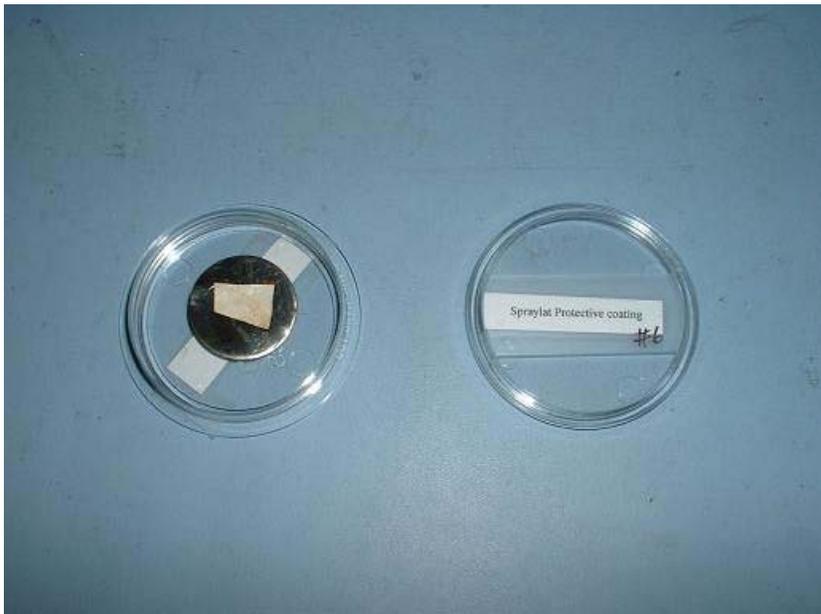


Raman spectrum of Boric Acid, taken
from the InSITE Raman Analyzer



Sample of Spraylat on steel

Spraylat Protective Coating



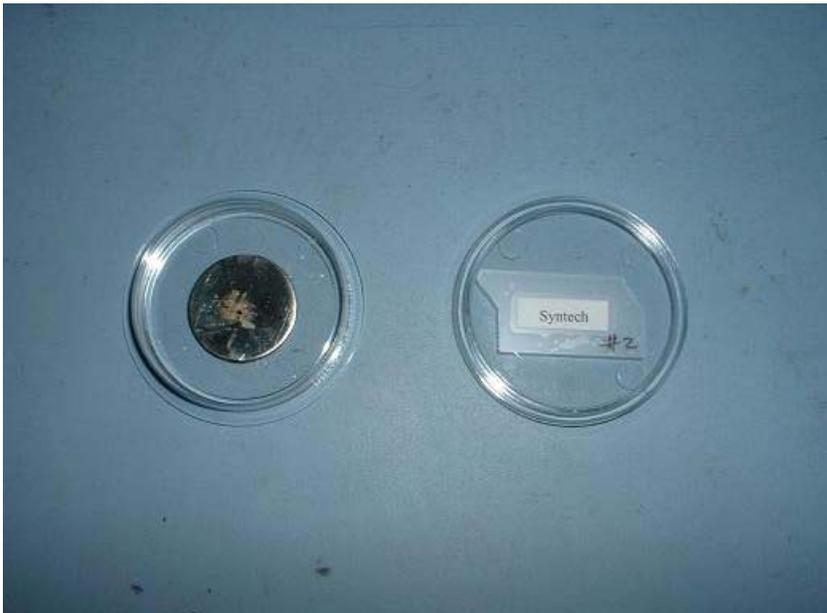
Raman/fluorescence spectrum of Spraylat Coating



Sample of dried decontaminant deposit on steel

Syntech: A decontamination agent used in power plant service

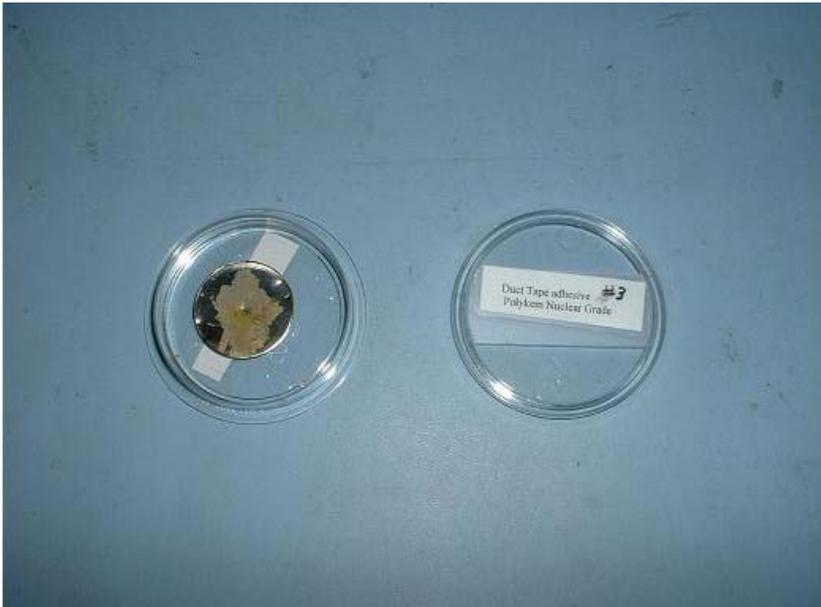
Fluorescence spectrum of Syntech



Sample of duct tape deposit on steel

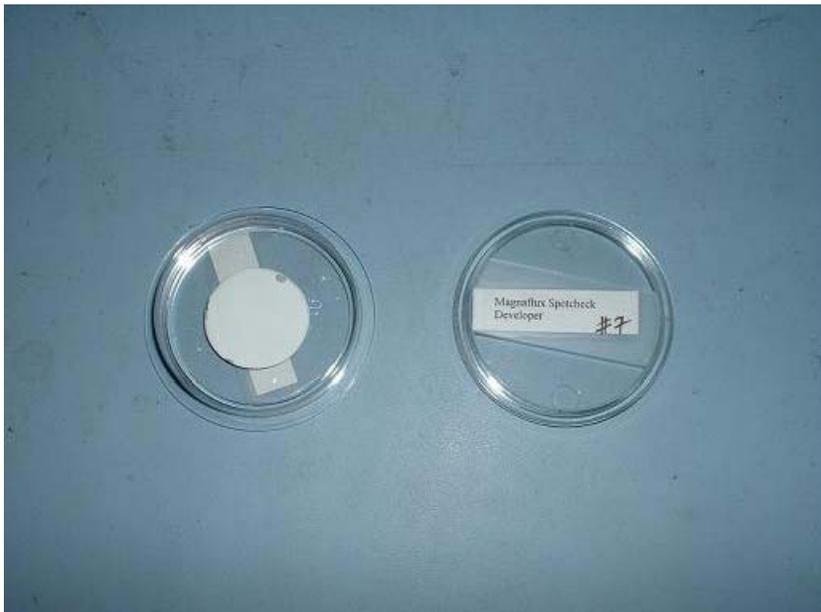
Duct Tape Adhesive: Nuclear Grade

Fluorescence spectrum of Duct Tape



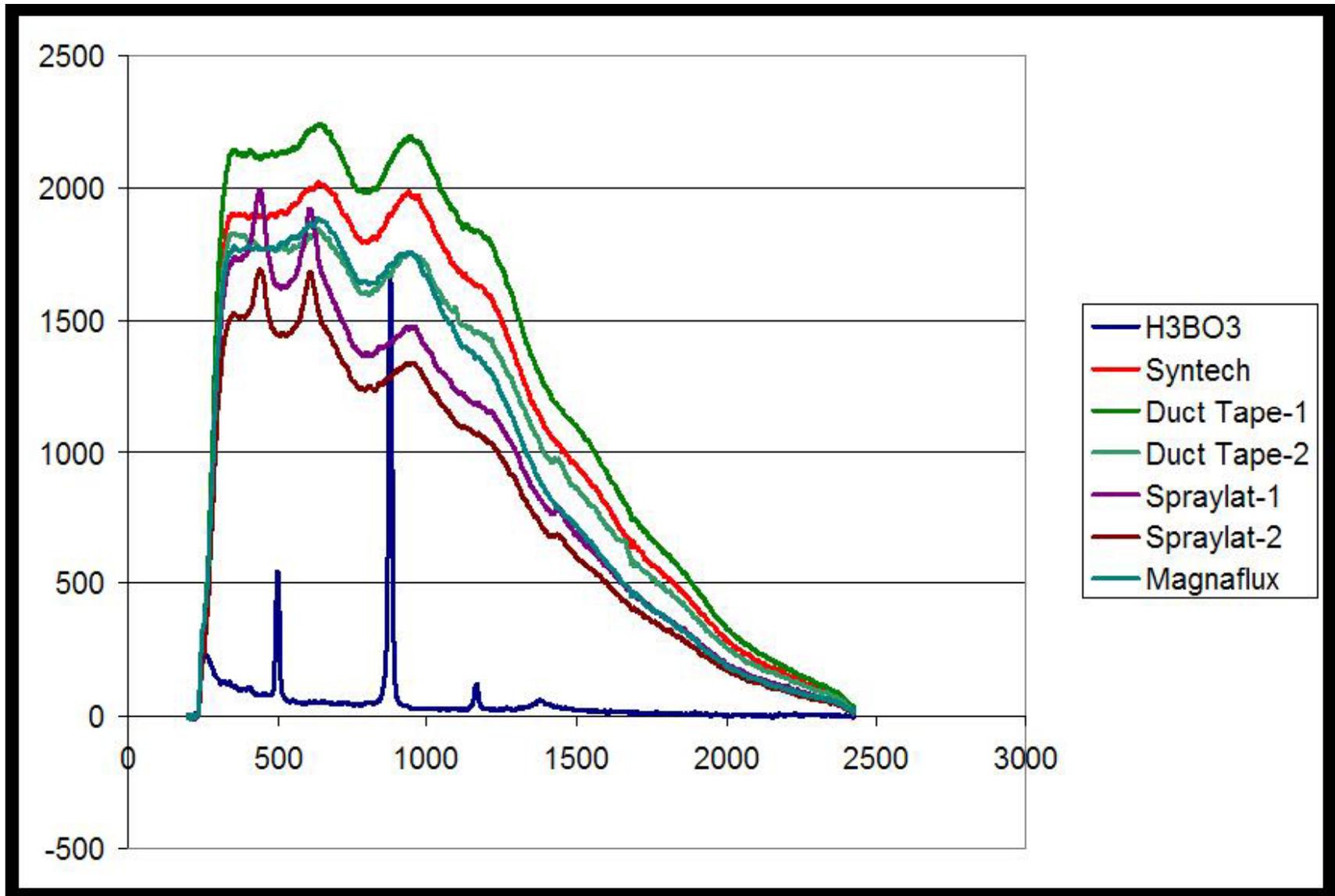
Sample of Magnaflux on steel

Magnaflux Spotcheck Developer



Fluorescence Magnaflux Spotcheck Developer

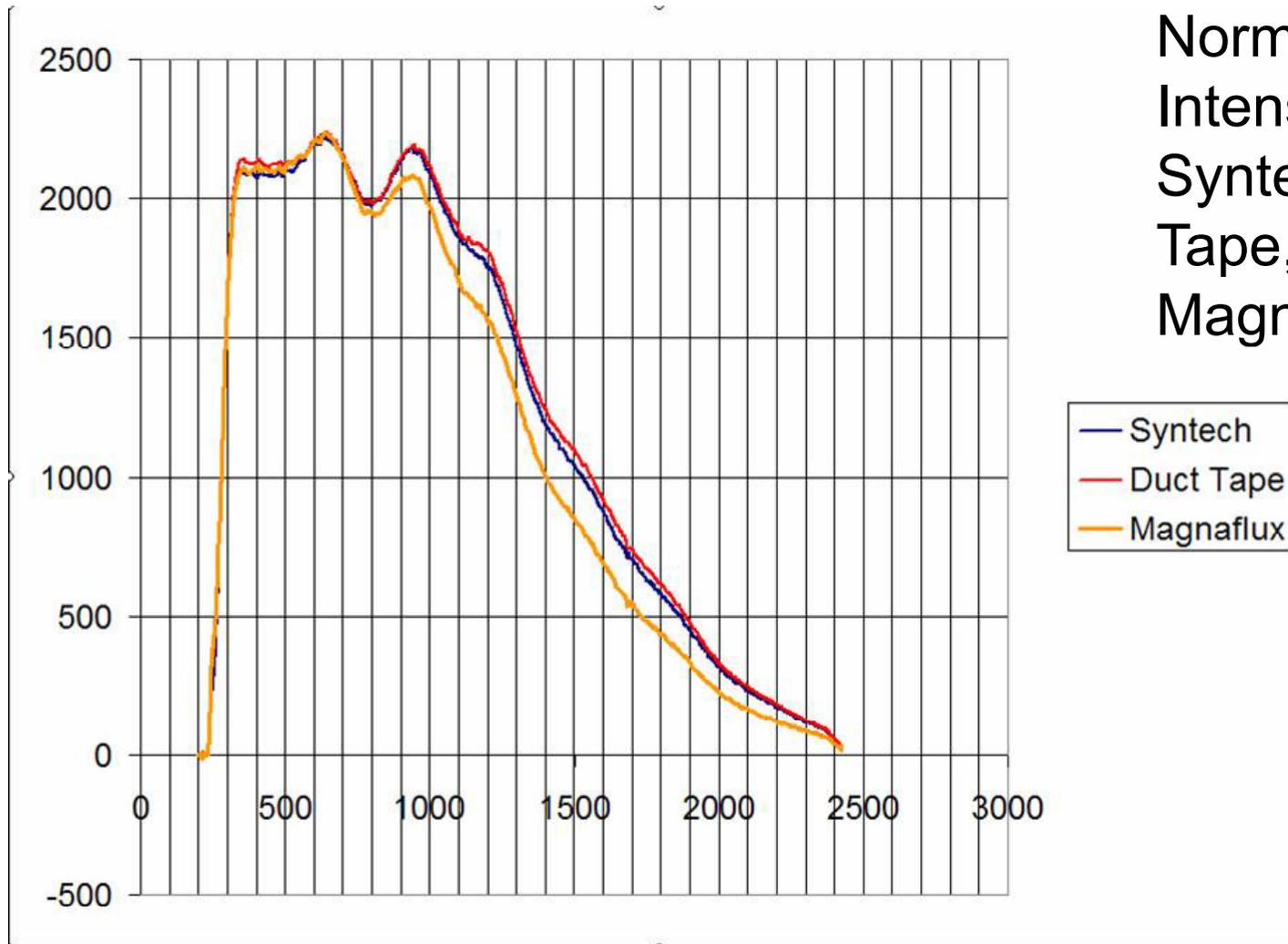




Differentiating Spectra

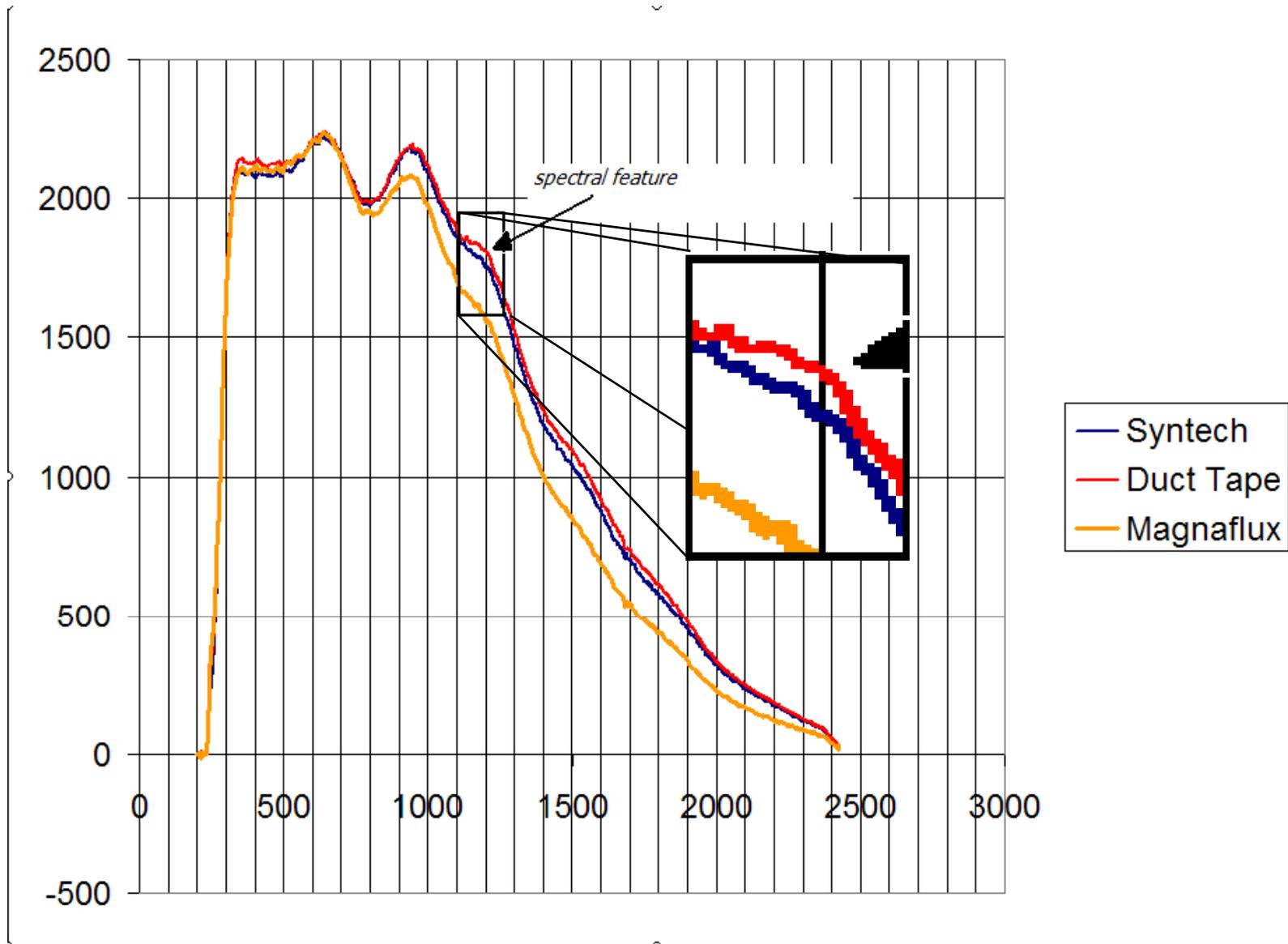
- Boric Acid shows clear Raman scattering with no fluorescence. Peaks are strong and clear at 500 cm^{-1} , 875 cm^{-1} , and 1170 cm^{-1} .
- Spraylat shows strong fluorescence with two superimposed peaks at 445 cm^{-1} and 634 cm^{-1} due to titanium dioxide.
- Syntech, Magnaflux and Duct Tape have strong fluorescence requiring closer examination.

Differentiating Materials



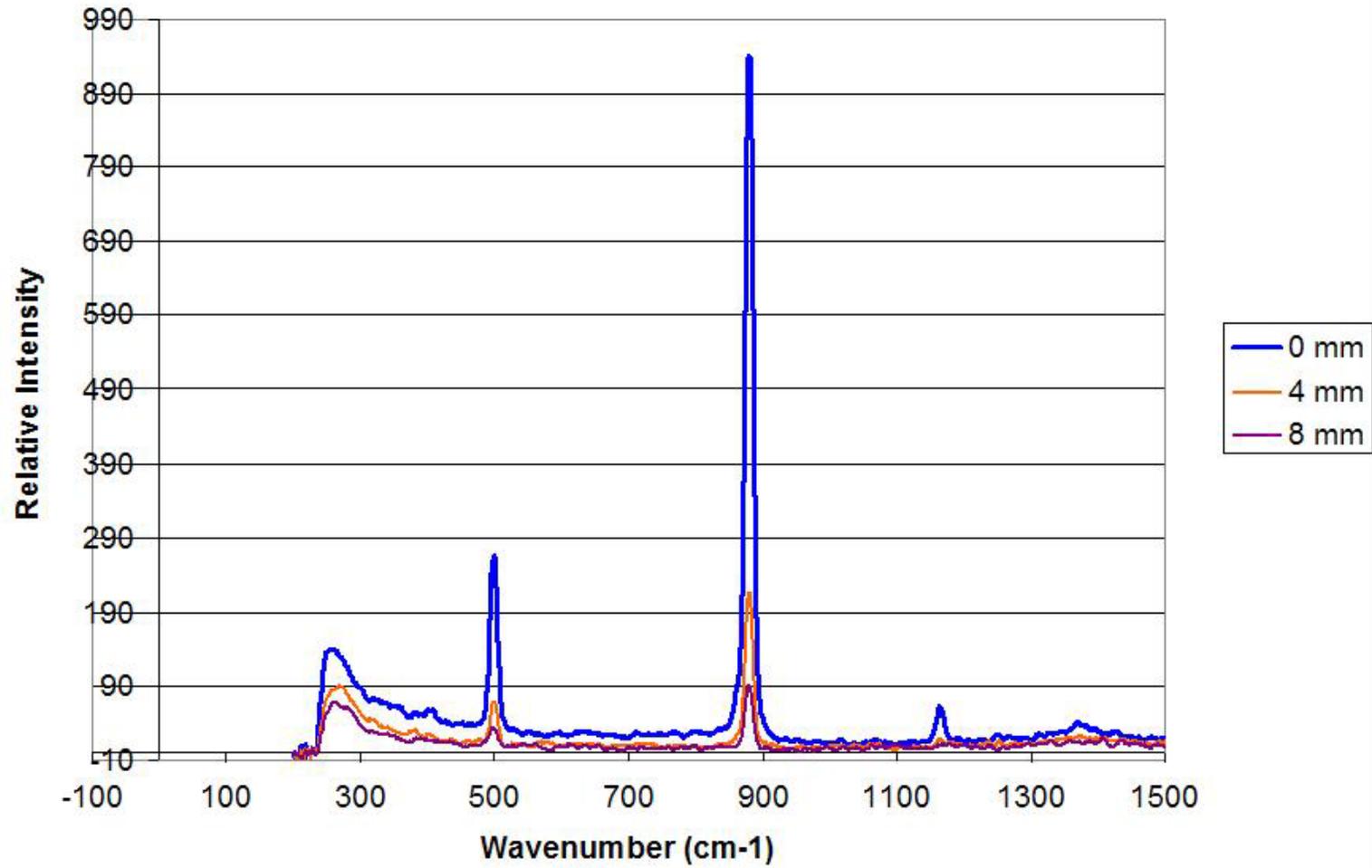
Interpretation of Fluorescence spectra

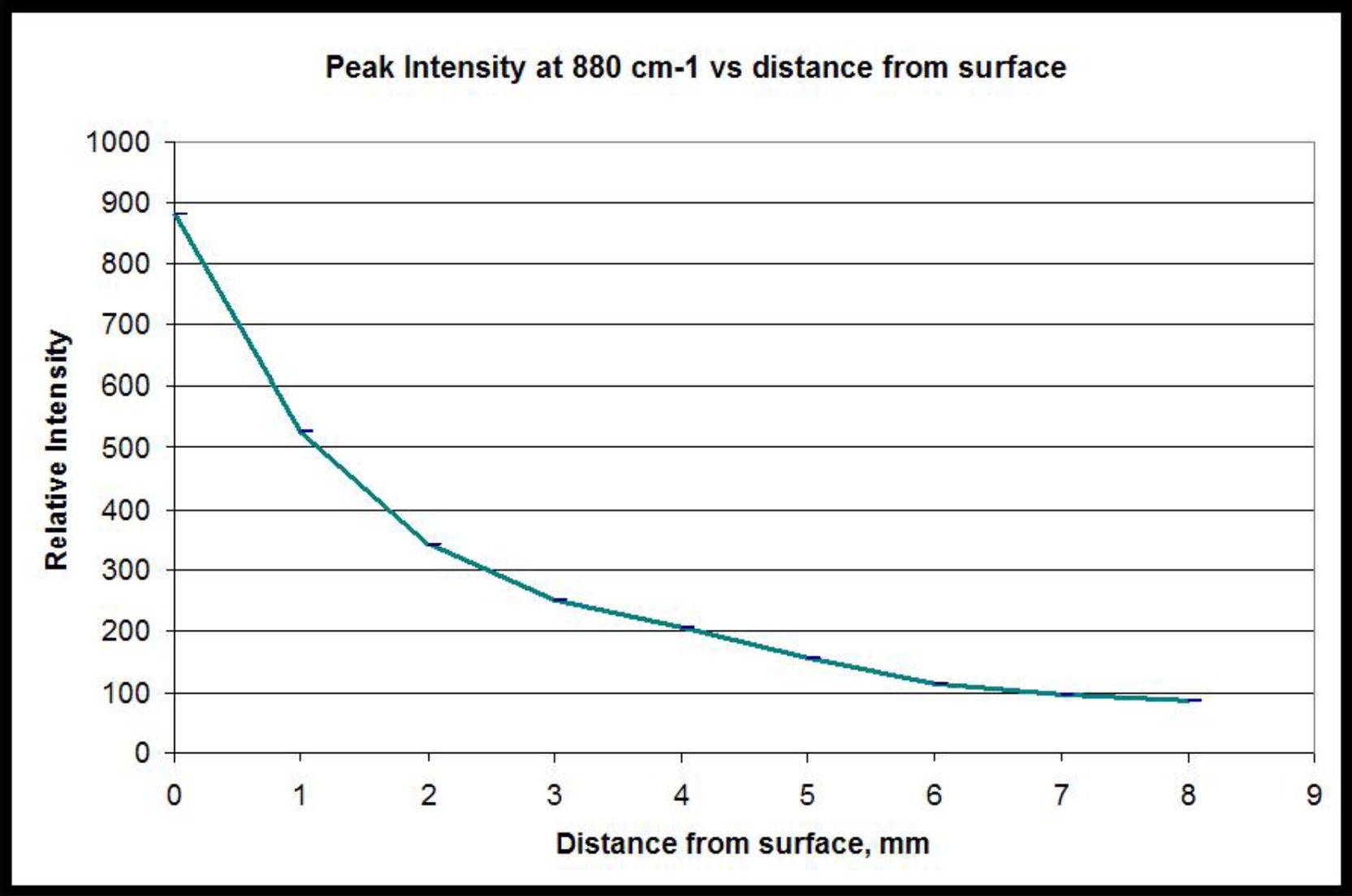
- Magnaflux: Ratio of peaks at 660 cm^{-1} and 960 cm^{-1} : 1.07
- Syntec ratio of these two peaks : 1.02
- Duct Tape ratio : 1.02
- Differentiating between Duct Tape and Syntec requires closer analysis.



Fluorescence spectra contain features which can be used to separate one material from another, although Raman is a more powerful tool

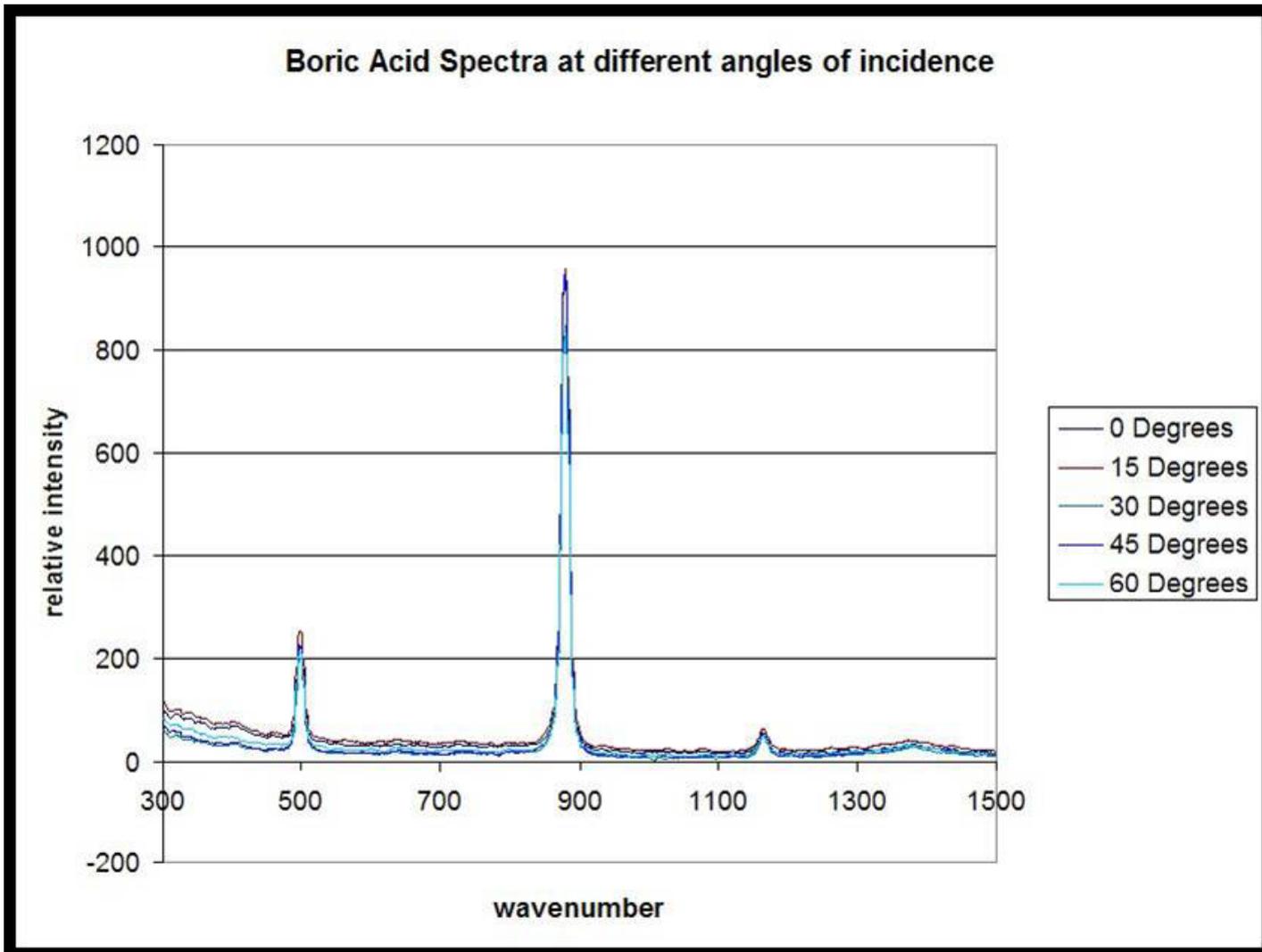
Boric Acid Spectra at different probe distances

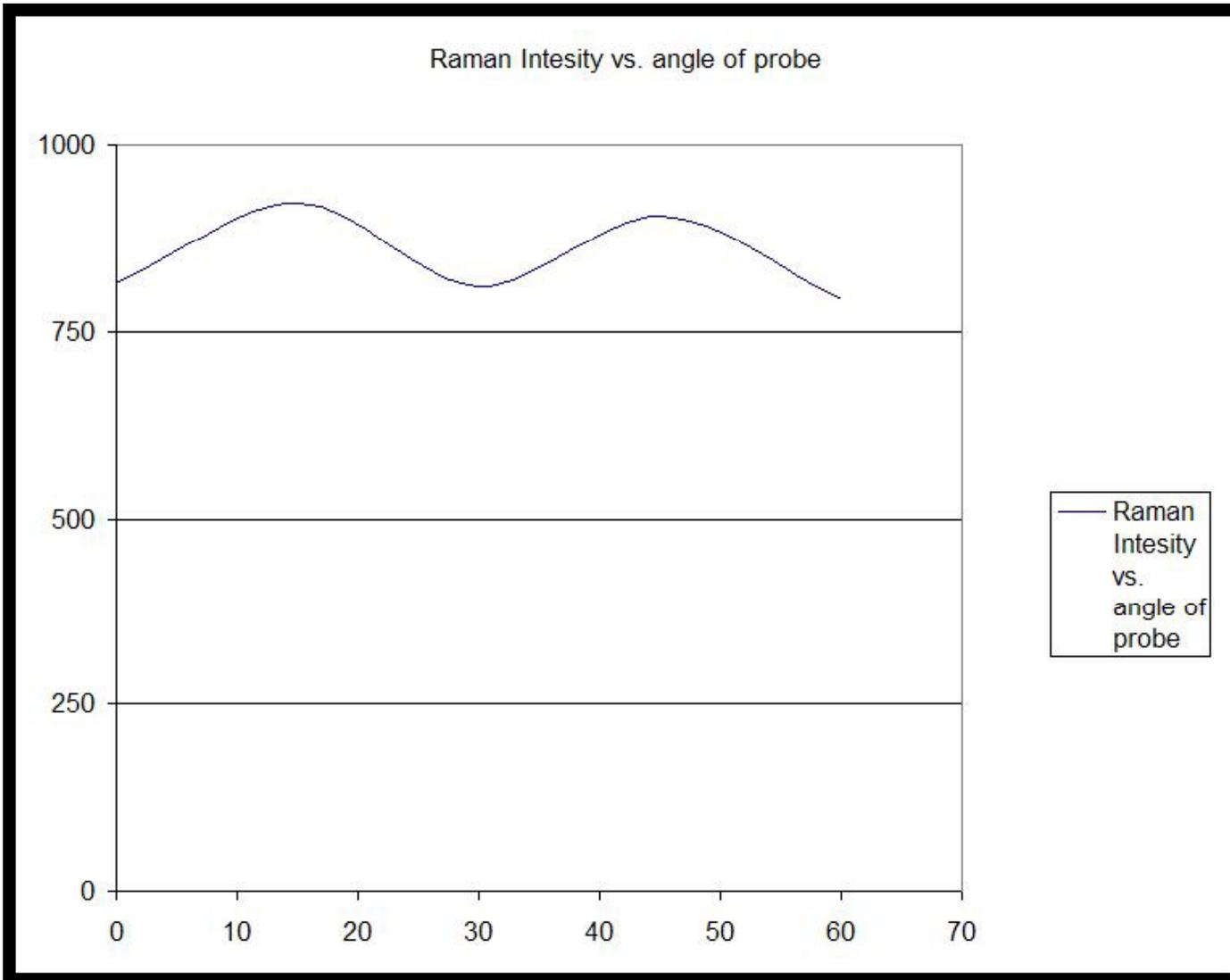




Intensity vs. distance of probe

- Intensity falls with distance from surface. This probe is optimized for contact.
- Different lenses can be used for non-contact applications.





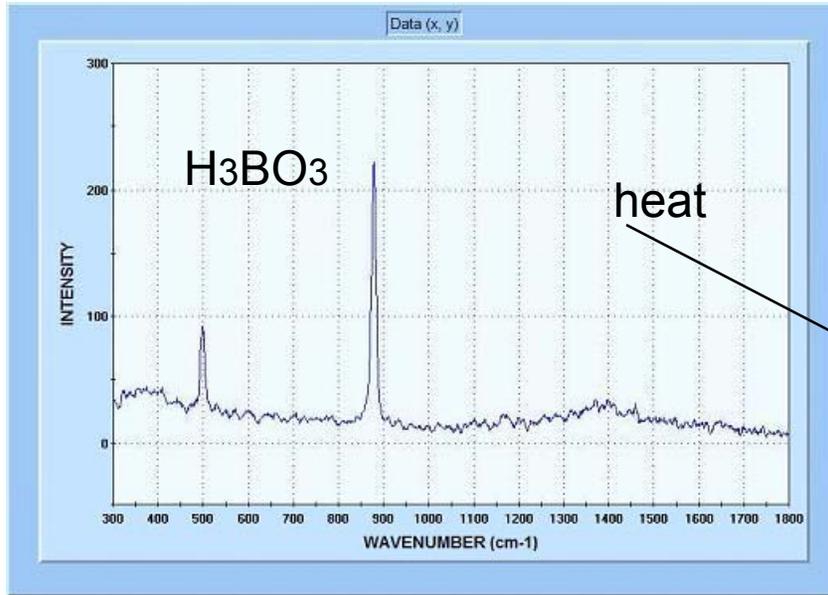
Intensity vs. probe angle

- In actual use it may not be possible to place a probe directly on the sample at a right angle.
- Since Raman is a scattering technique (not a reflectance technique) there is no significant loss of signal.
- Reflected laser is reduced when an oblique angle is used, giving a reduction in stray light and improved signal to noise.

H_3BO_3 (ortho boric acid) vs. HBO_2 (meta boric acid) in RCS deposits

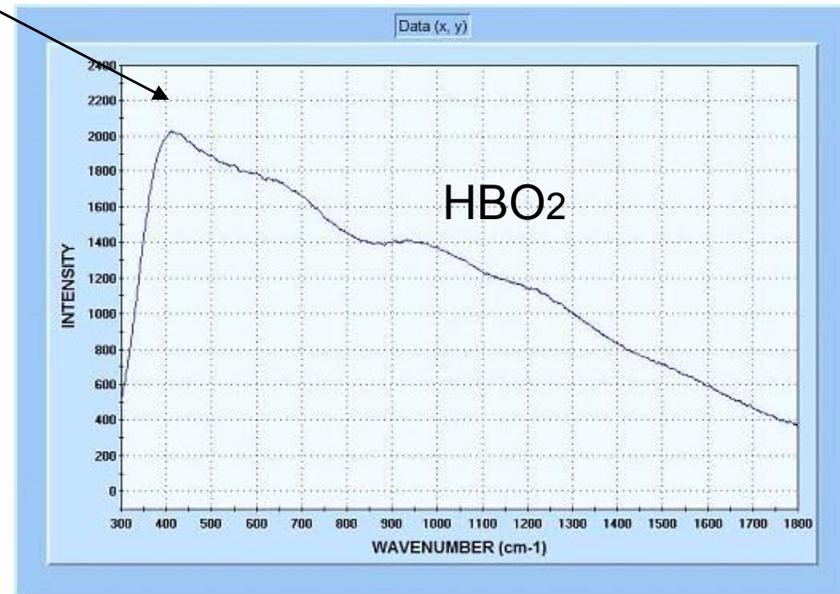
- Boric Acid is found in two forms, ortho boric acid and meta boric acid.
- Orthoboric acid (sassolite) shows good Raman peaks, however heating it to high temperatures will cause decomposition to metaboric acid (metaborite).
- Metaborite has strong fluorescence and no Raman peaks
- Metaborite can be converted back to orthoboric acid by adding moisture.

H₃BO₃ (ortho boric acid) vs. HBO₂ (meta boric acid)



Left: RCS, dried at 100°C. (Li:B ratio 5:100)

Right: RCS, dried at 100°C. Then heated to dehydrate (>169°C)

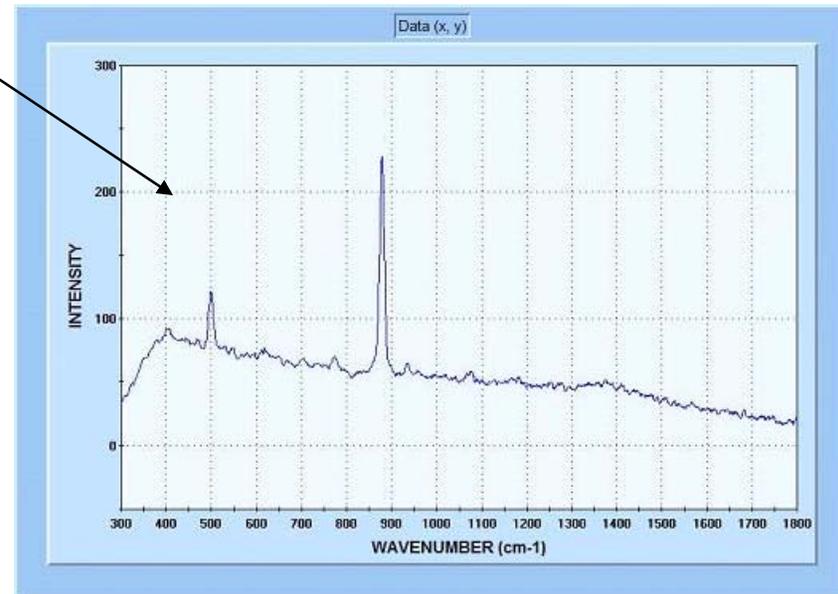


H₃BO₃ (ortho boric acid) vs. HBO₂ (meta boric acid)



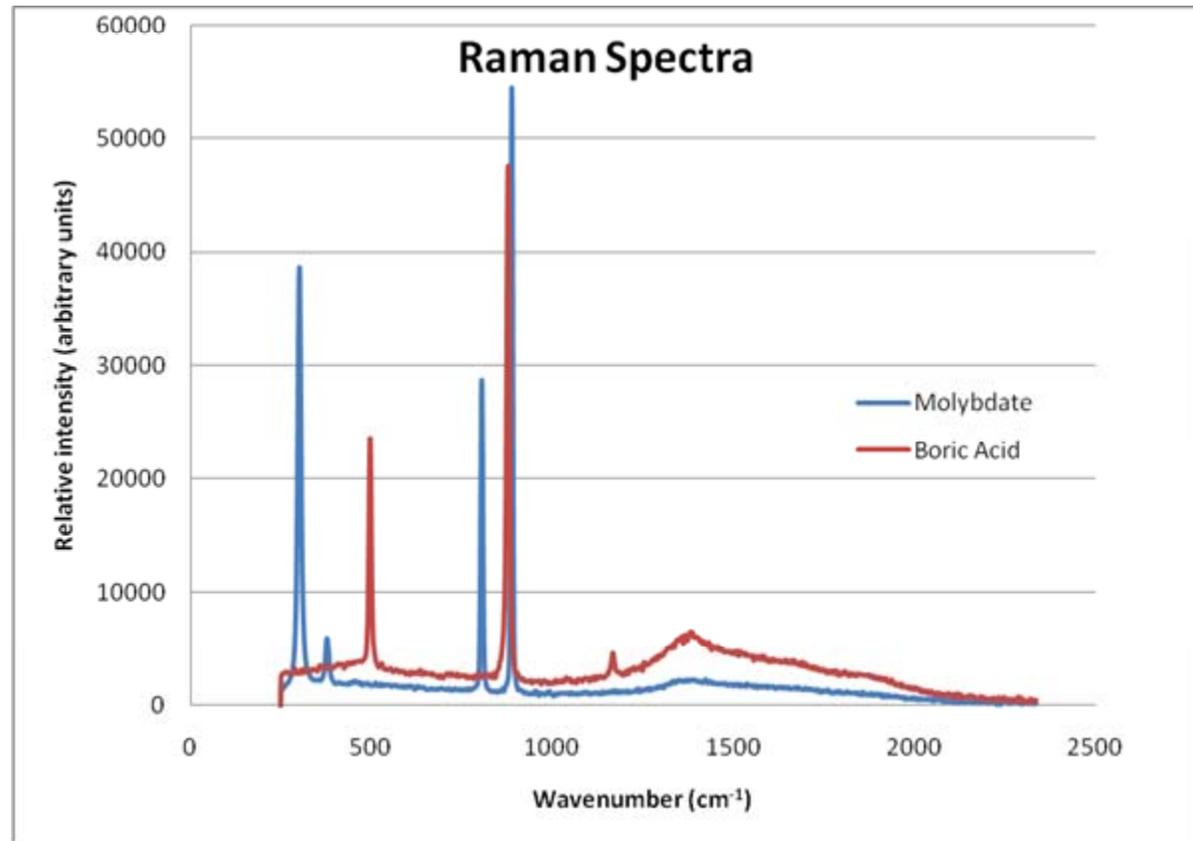
Left: RCS, dehydrated at >169°C.

Right: RCS, dried at 100 degrees C, heated to dehydrate, then treated with liquid water (aerosol spray)—similar results occur when sample absorbs moisture from humid air.



Primary coolant vs. secondary coolant spills

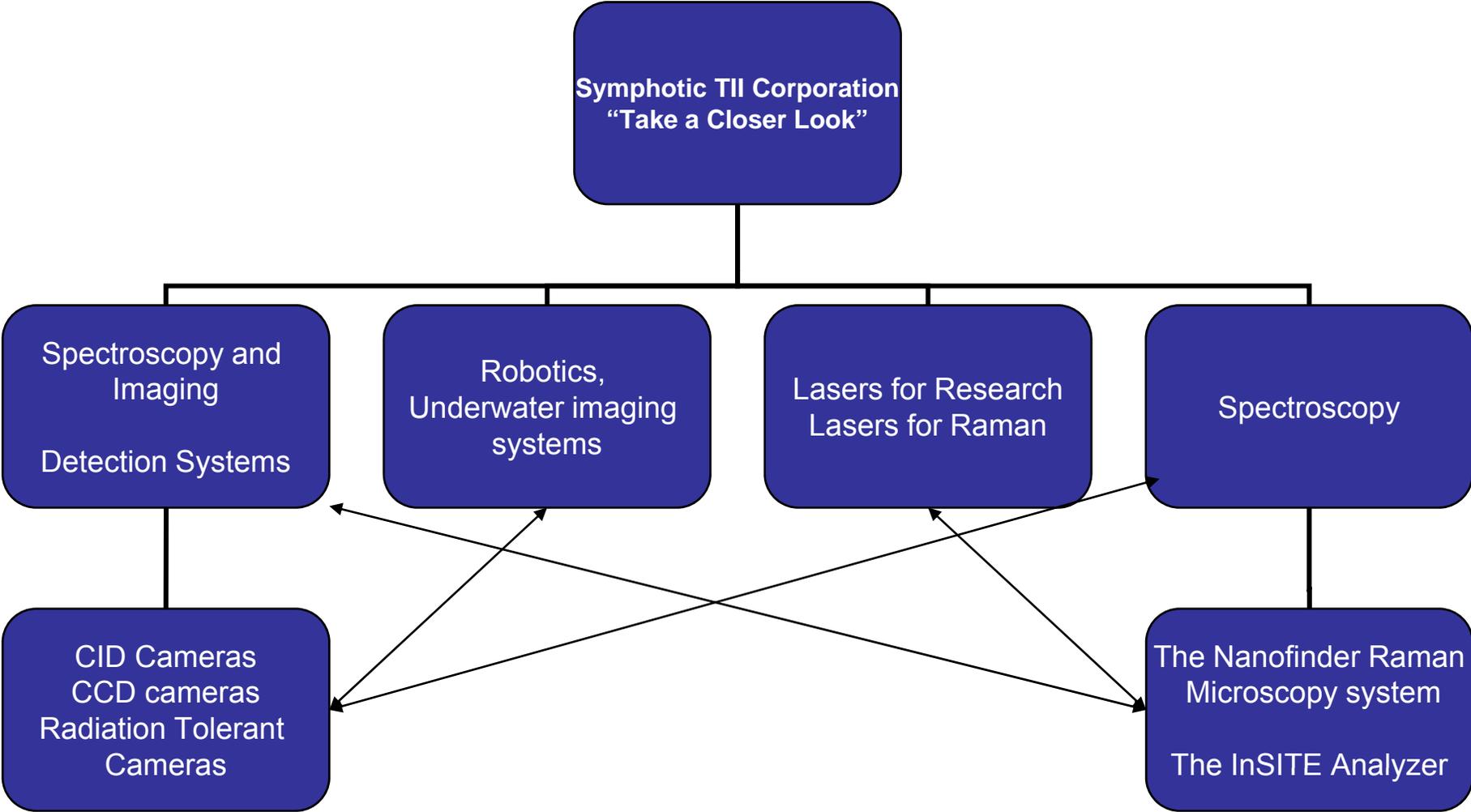
- The InSITE can also be used to distinguish primary coolant spill residues (which are mostly boric acid) from secondary spill residues, (which are mostly sodium molybdate).



Conclusion

- The InSITE™ Analyzer is a proven tool for determining the chemical composition of stains and deposits in nuclear power plants
- The InSITE™ Analyzer is especially useful for verifying the presence of boric acid deposits and sodium molybdate deposits.
- The InSITE™ Analyzer shows flexibility in probe positioning for Raman Determinations.
- The InSITE™ Analyzer can determine the form of boric acid: meta or ortho, and thereby provide an indication of the heating and moisture environment in which the sample was formed.
- The InSITE™ Analyzer is part of a program by the In Service Inspection Group at PVNGS to provide a conclusive way to identify boric acid deposits, and eliminate the need and risk involved with sample removal from in containment.

Symphotonic TII's Role



Symphotic TII Corporation manufactures the world's only high radiation underwater, color, solid state cameras—The AquaRAD®—and distributes other imaging and robotics products for the nuclear power industry.

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References

- The Behavior of Light Water Reactor Fuels, 4th edition (*Kaisuiro Nenryo no Furumai*), Japan Nuclear Energy Safety Research Association: July, 1998, p.336
- Operational Experience and Further Development of Water Chemistry of Nuclear Power Plants, Atomic Energy Society of Japan: June, 1995

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