Pervasive Spectral Sensing

Modern Raman Spectrometers: Cutting Edge Technology in The Palm of Your Hand

CPSC Symposium on Phthalate Screening and Testing

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March 1, 2012

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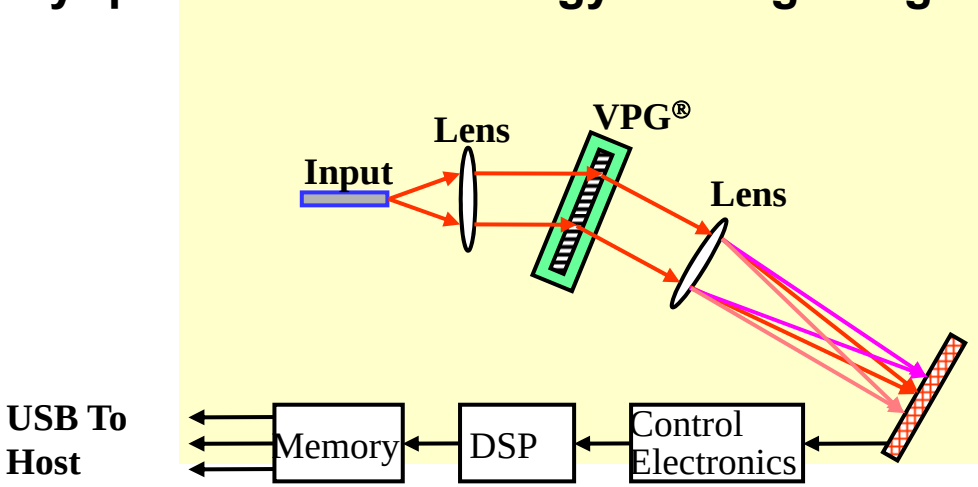
BAYSPEC

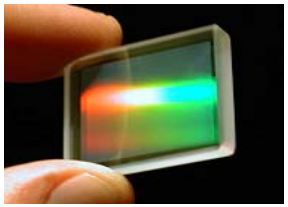
Who We Are

- BaySpec, Inc.
  - Founded in 1999
  - 25 employees located in San Jose, CA
  - In-house Volume Phase Grating (VPG®) production
  - World leader in miniaturization of spectrometers (UV/VIS/NIR)
- Rigaku, Inc.
  - Founded in 1951
  - Over 1,100 people worldwide in operations based in Japan, the U.S., Europe and China
  - World leaders in the fields of protein and small molecule X-ray crystallography, general X-ray diffraction, X-ray spectrometry, X-ray optics, semiconductor metrology, automation, computed tomography, nondestructive testing and thermal analysis.
  - Rigaku Raman Technologies, Inc. (RRT) Founded in 2011

What We Do

BaySpec's core technology is our grating fabrication lab





Volume Phase Grating®

- **F/2 optics**
- **Span: 400 nm-2250nm**
- **Athermal design**
- **0-50 deg C operations**
- **Wavelength fully calibrated before devices leave factory**

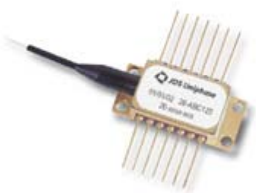
Major Design Considerations

- ***No moving parts; Designed to produce in volume***
- ***Environmentally insensitive***
  - ***Our Heritage is in telecom with over 30,000 units in the field***
  - ***Several hundred Raman spectrometers to date***

Enabling Technologies

Multi-disciplinary technology advancements make the miniaturization of spectral sensors possible today

- ***Miniature High Efficiency Lasers***
- ***Holographic Optical Elements***
- ***Low Cost, Sensitive Solid State Detector Arrays***
- ***Cheaper, Faster Computer Chips***



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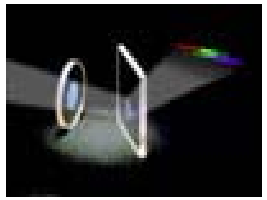

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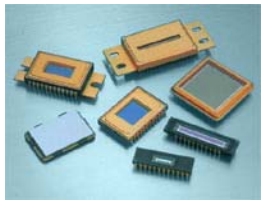

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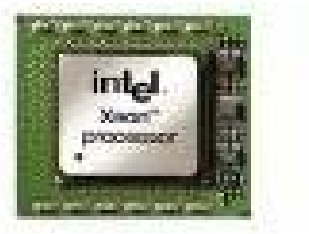

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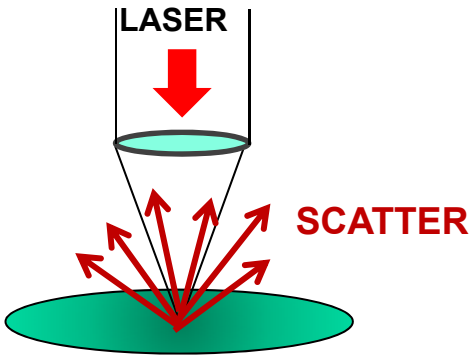
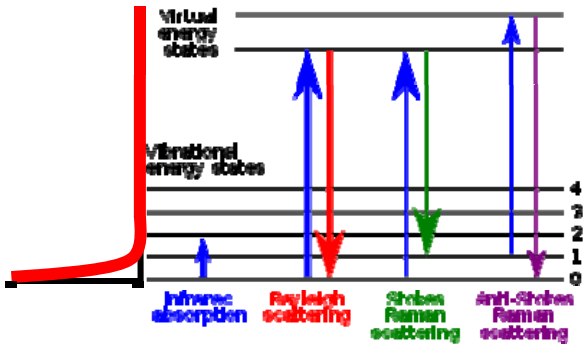
Raman Spectroscopy

- Shine monochromatic laser light onto a material and collect the scattered photons that gain or lose energy to molecular vibrations
- 1 in10^6 photons scatters inelastically
- Signal strength goes as $(1/\lambda_{LASER})^4$
- High degree of chemical specificity
- No sample preparation
- Immune to the presence of water





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Raman Fingerprints – Chemical Specificity

Bond	Compound type	Frequency range cm^{-1}
C—H	Alkanes	2850–2960 1350–1470
C—H	Alkenes	3020–3080 675–1000
C—H	Aromatic rings	3000–3100 675–870
C—H	Alkynes	3300
C=C	Alkenes	1640–1680
C≡C	Alkynes	2100–2260
C⋯C	Aromatic rings	1500, 1600
C—O	Alcohols, ethers, carboxylic acids, esters	1080–1300
C=O	Aldehydes, ketones, carboxylic acids, esters	1690–1760
O—H	Monomeric alcohols, phenols	3610–3640
	Hydrogen-bonded alcohols, phenols	3200–3600
	Carboxylic acids	2500–3000
N—H	Amines	3300–3500
C—N	Amines	1180–1360
C≡N	Nitriles	2210–2260
$—NO_2$	Nitro compounds	1515–1560 1345–1385

The majority of compounds have vibrational frequencies between 500 and 1800 cm^{-1}

- **Nitriles and isocyanides around 2200-2300 cm^{-1}**
- **Alkynes (carbon-carbon triple bonds) around 2100-2200 cm^{-1}**
- **NH, CH, OH bonds > 2800 cm^{-1}**

- **Sulfur-oxygen (sulfates, sulfonates, etc., carbon-oxygen (carbonates), nitrogen-oxygen (nitrates, nitrites), oxygen-oxygen (peroxides) below 1850 cm^{-1}**

Simple bonds have specific frequencies, but molecules made up of these bonds interact to produce spectra with unique fingerprints below ~1800 cm^{-1}

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The Fluorescence Issue

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- **Raman Sensitivity**
  - **1 in 1,000,000 photons scattered inelastically**
  - **Fluorescence ~ 1,000,000 stronger than Raman Scattering**

  ⇒Ppm levels of fluorophores will compete with Raman Scattering

With longer laser wavelengths there is less likelihood of absorption

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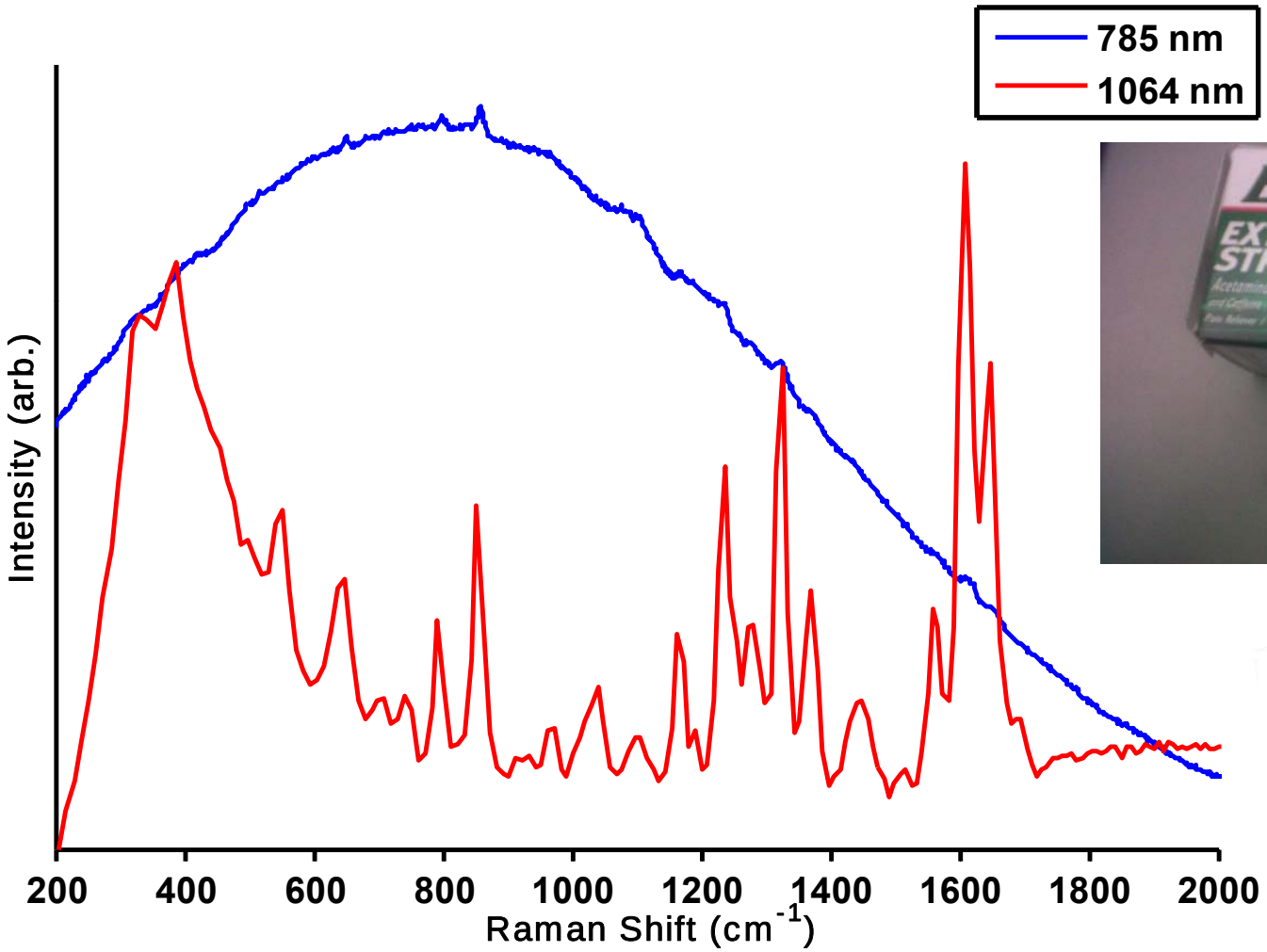
Raman Excitation

- Most molecules have absorption energies in the UV and Visible wavelength regions
- 514.5 nm (Argon ion laser) and 532 nm (Nd: YAG laser) – Strong scattering, but a lot of materials fluoresce
- 785 nm (Diode laser)
  - Many more chemicals can be measured
- 1064 nm (Fiber)
  - Further reduces fluorescence
  - Must use an InGaAs array instead of a CCD array detector (This is a big BaySpec advantage)

The 1064nm Advantage



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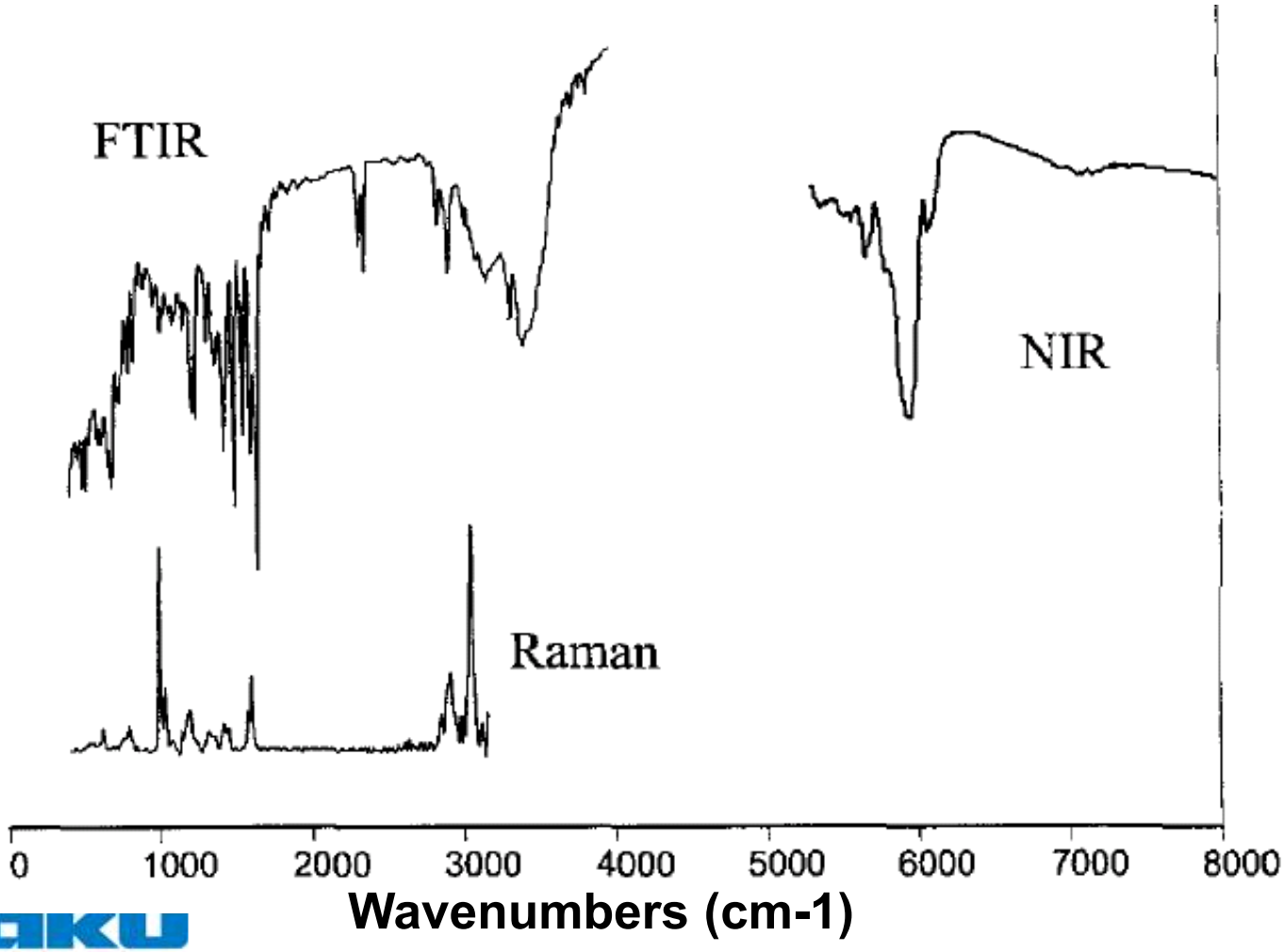
Raman: High Degree of Chemical Specificity

polystyrene



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Pure Materials are Easily Distinguished

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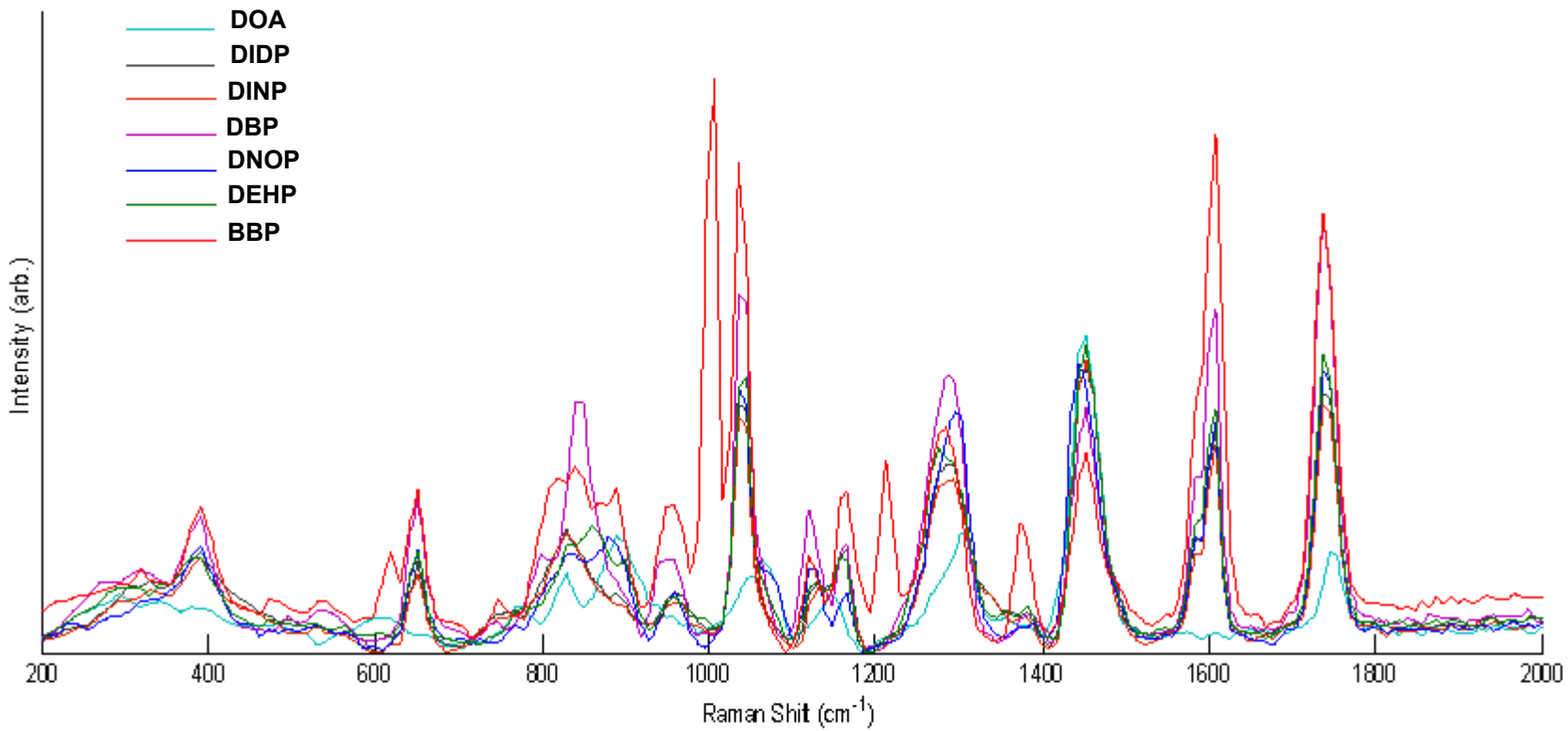
1064 nm Handheld Raman Spectrometer



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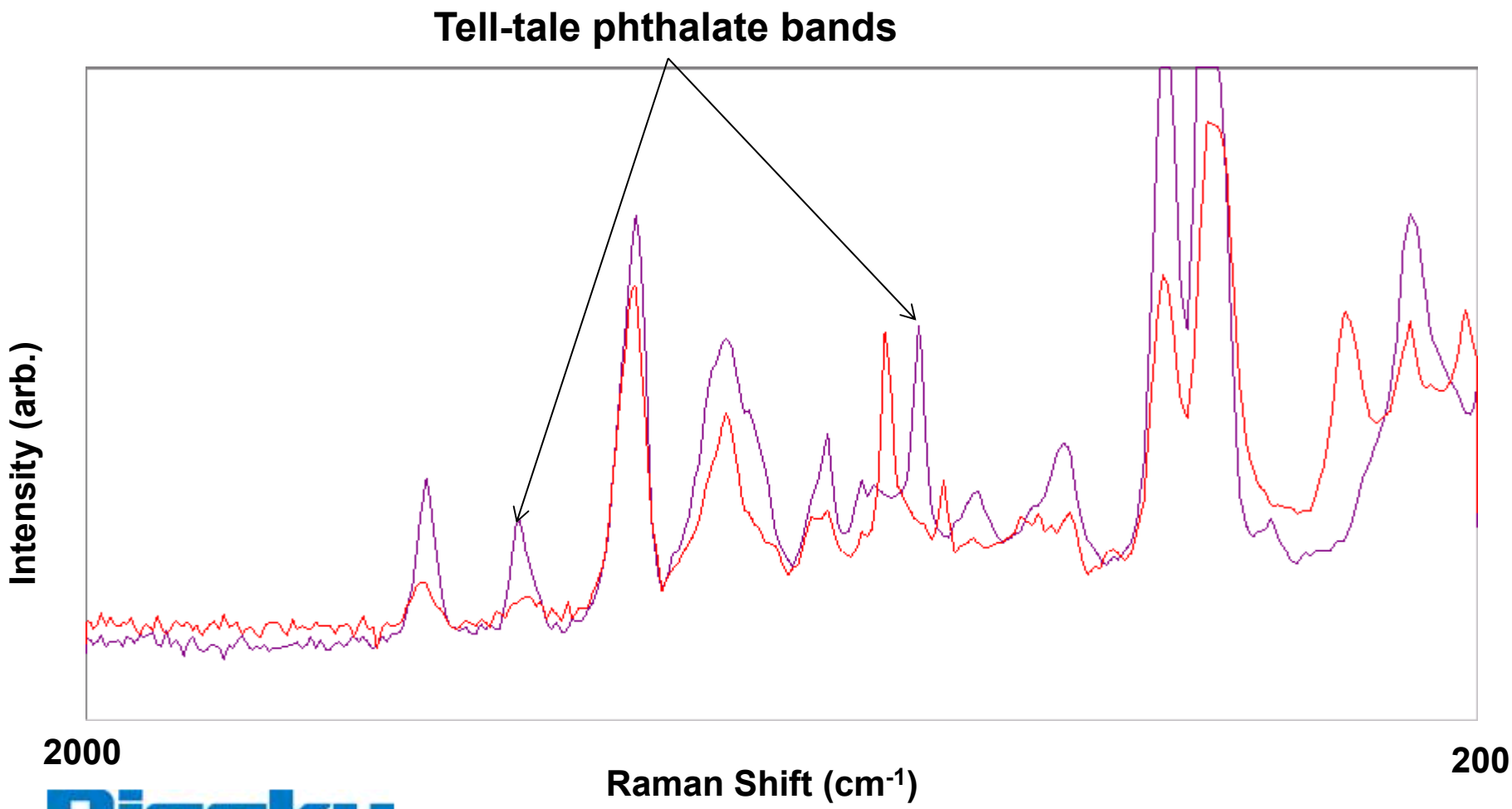
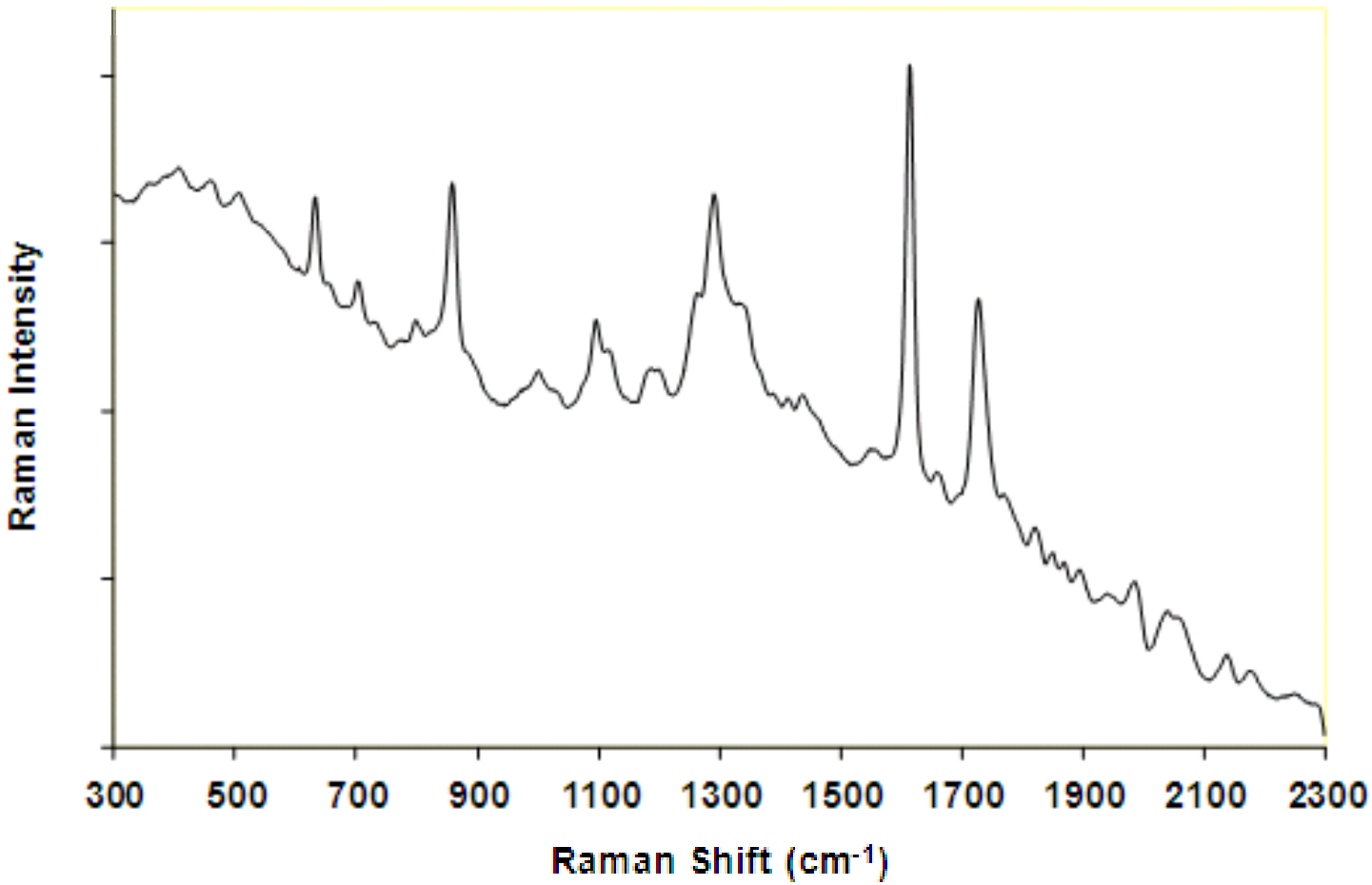
PVC w/DOA and DEHP



Automated Library Searching

Raman spectrum of a plastic soda bottle



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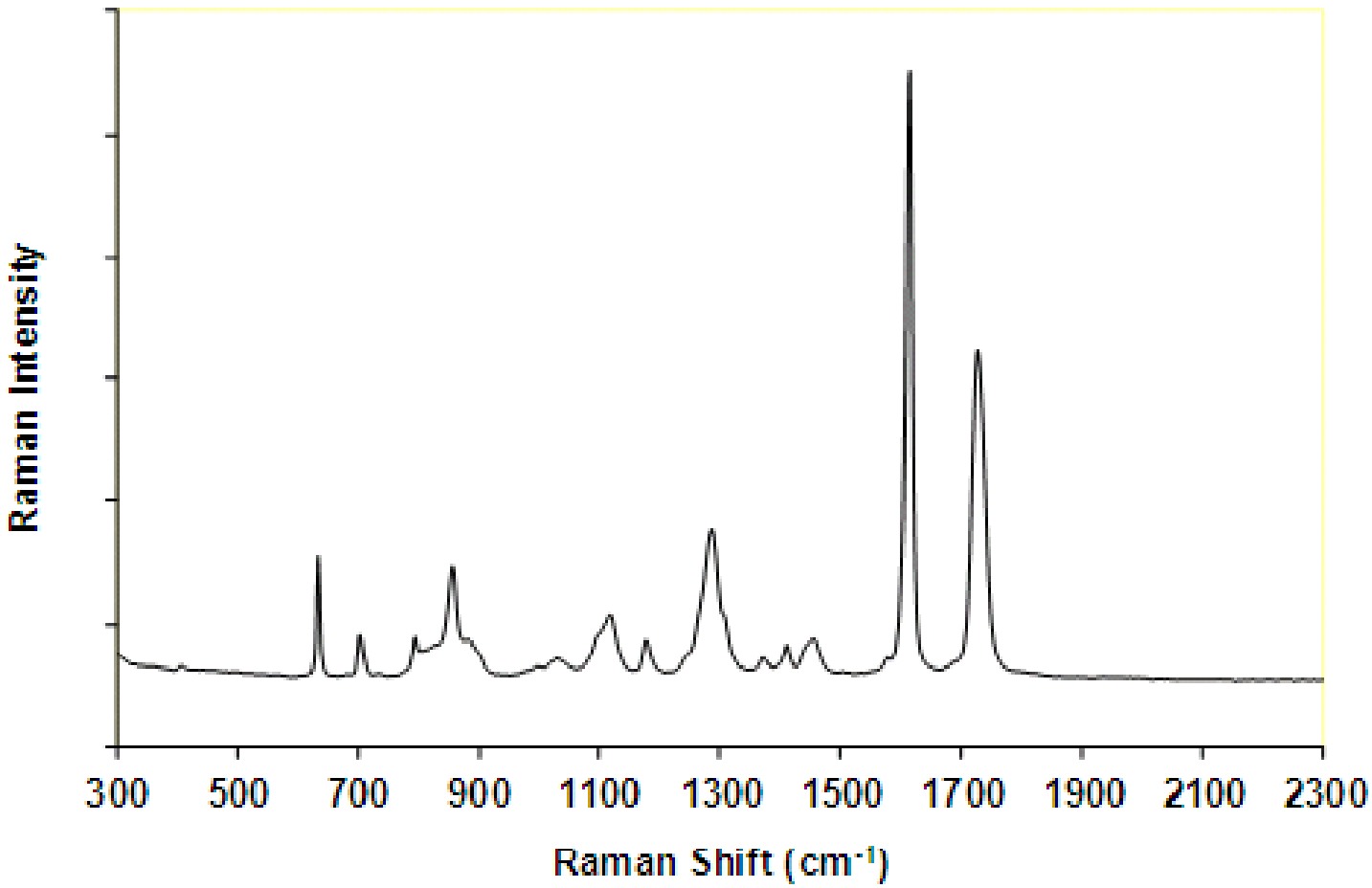
Clear Plastic From Soda Bottle

Best Match From Raman Library : Poly(ethylene terephthalate)



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Raman Hand-Held Spectrometers

- **Family of portable/hand-held Raman Analyzers**
  - **Xantus-0**
  - **Xantus-1**
  - **Xantus-Mini**
  - **FirstGuard™**

Xantus-0

Xantus-Mini

Xantus-1

FirstGuard™

Accessories

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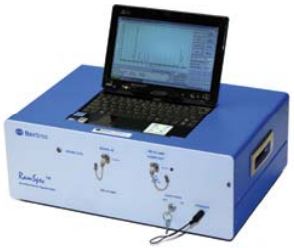
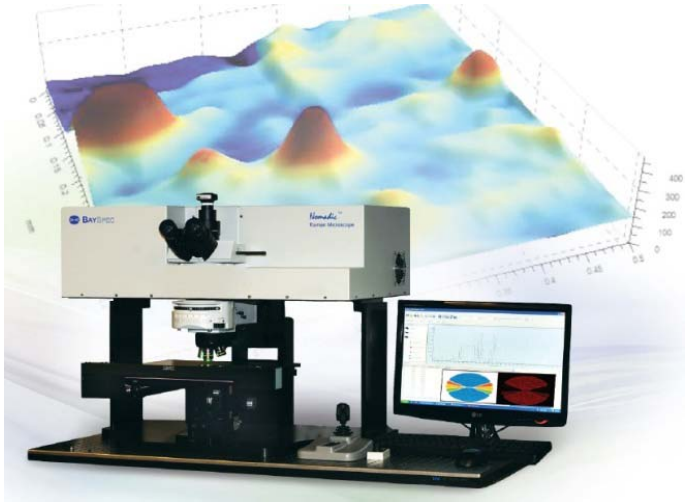
Benchtop Raman Spectrometers and Microscopes

633/785nm Raman Instrument "Portability"



532/785/1064nm Raman Instrument "RamSpec"

532/785/1064nm Raman Microscope "Moving Lab"



532/785/1064nm Single/Double/Triple Wavelength Raman Microscope "Nomadic"

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More portable Raman Spectrometers

- **Shhhh…**
  - **Visit the Rigaku booth at Pittcon in Orlando, FL March 11-15, 2012 to see next generation dual-wavelength handhelds (Xantus and FirstGuard)**

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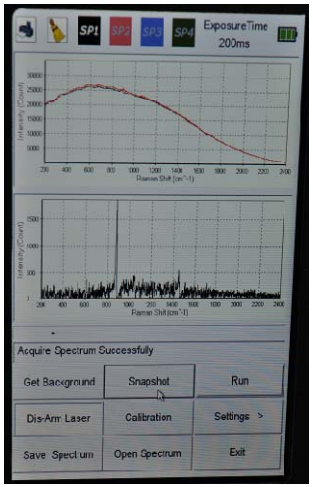
Next Generation Systems

- **Shifted Excitation Raman Difference Spectroscopy (SERDS)**
  - **Collect two spectra from closely spaced laser wavelengths (~785nm) and subtract to obtain a pseudo-derivative spectrum**
  - **1st Unit built and in testing at the factory (Xantus-1 style format)**



- **Spatially Offset Raman Spectroscopy (SORS)**
  - **Subsurface spectra (i.e., Depth Profiling)**
  - **1st unit undergoing alignment at the factory (not quite a hand-held…yet! (~12”x18”x6”)**

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