From Light Comes Illumination

Fourier transform infrared spectroscopy (FTIR) and Raman Spectroscopy

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IR and Raman

- Infrared and Raman spectroscopy are two of the most widely used techniques for the determination of molecular structure and the identification of compounds
- Sample handling is generally simple and usually non-destructive

IR and Raman

- ambient condition techniques – no vacuum
- depth of penetration of the technique is dependent on the accessory used to collect the data (FTIR)
- spatial resolution dependent on the type of experiment and the microscope, for Raman it can be as small as 1 micron, for FTIR it is approximately 20 microns
- Raman is sensitive to homo-nuclear and non-polar bonds (S-S, C-C, Se-Se)
- FTIR is sensitive to hetero-nuclear functional groups and polar bonds (C=O)

IR and Raman

- Both provide information on molecular vibrations.
- Why choose one over the other?
  - FTIR is the default – it is more common, has more accessible libraries and one always gets a spectrum
  - Why use Raman then?
    - **has a much better spatial resolution**
    - **is sensitive to some bonds that are not IR active**
    - **is sensitive to changes in crystal structure**
    - **can easily obtain spectra below 400 cm^{-1}**

Raman and FTIR Spectra

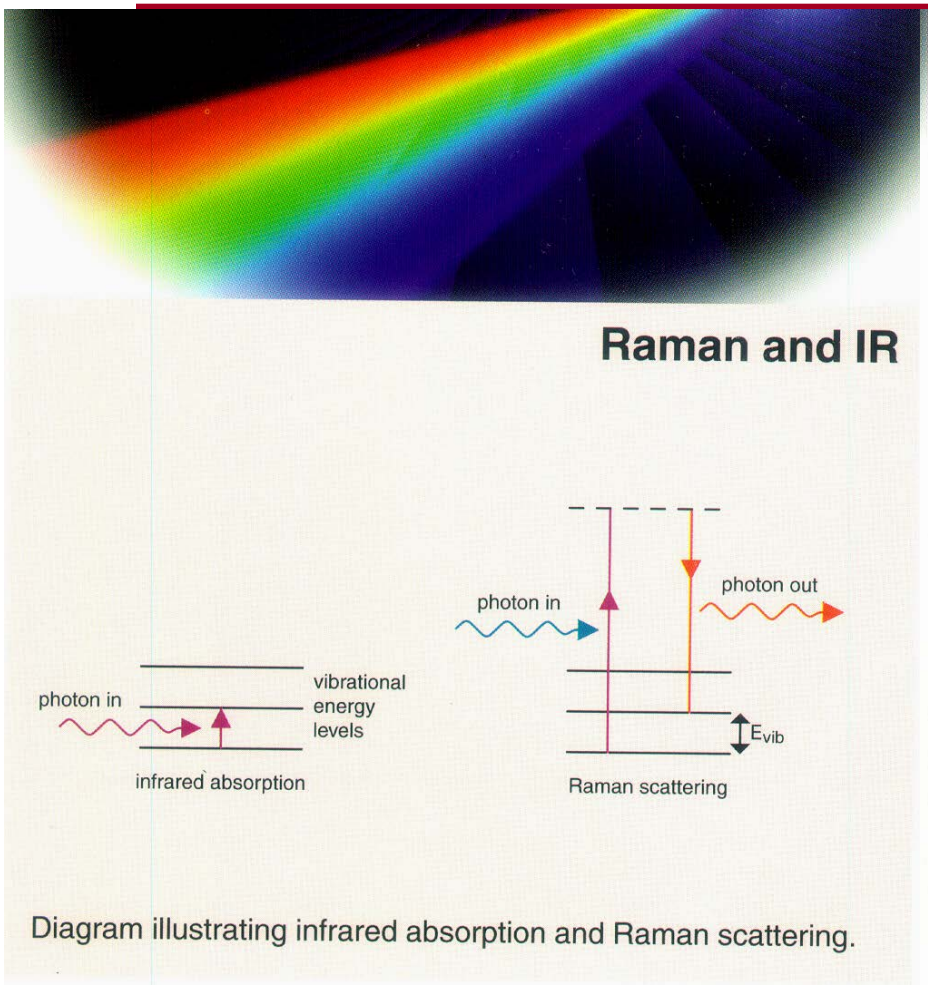
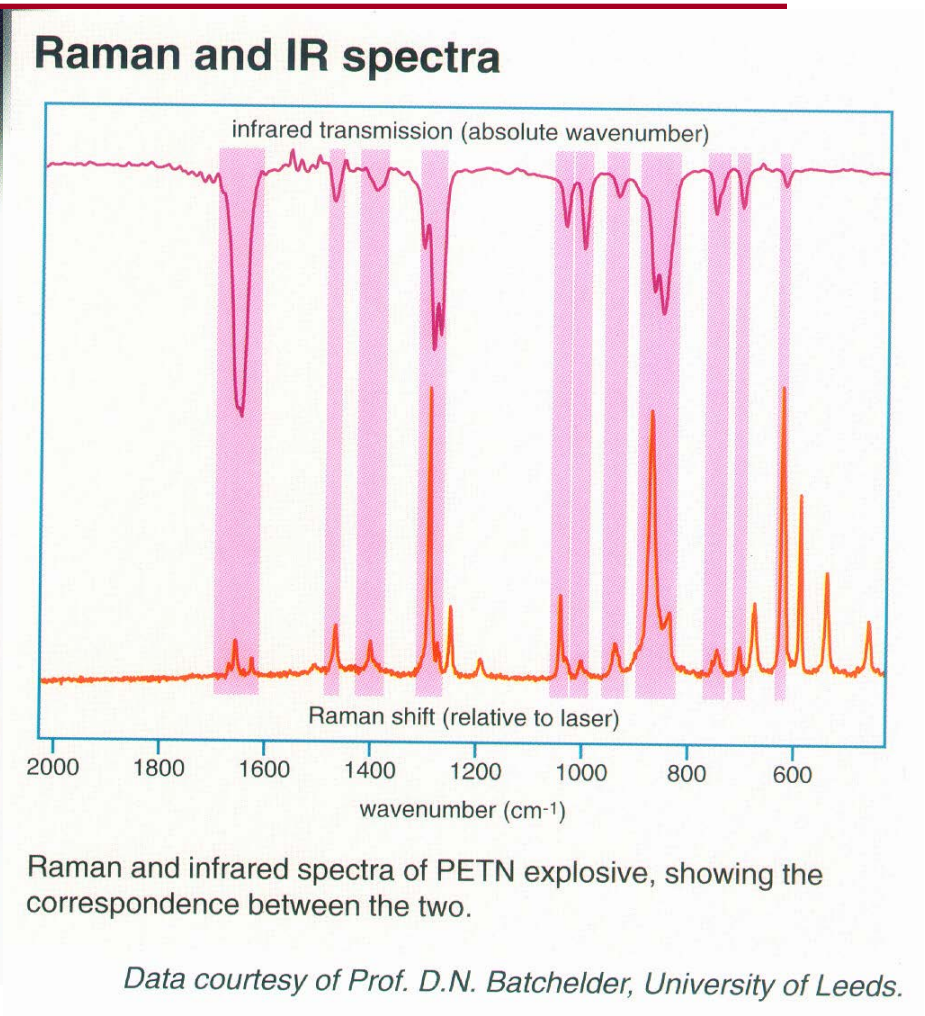


Diagram illustrating infrared absorption and Raman scattering.



Raman and infrared spectra of PETN explosive, showing the correspondence between the two.

Data courtesy of Prof. D.N. Batchelder, University of Leeds.

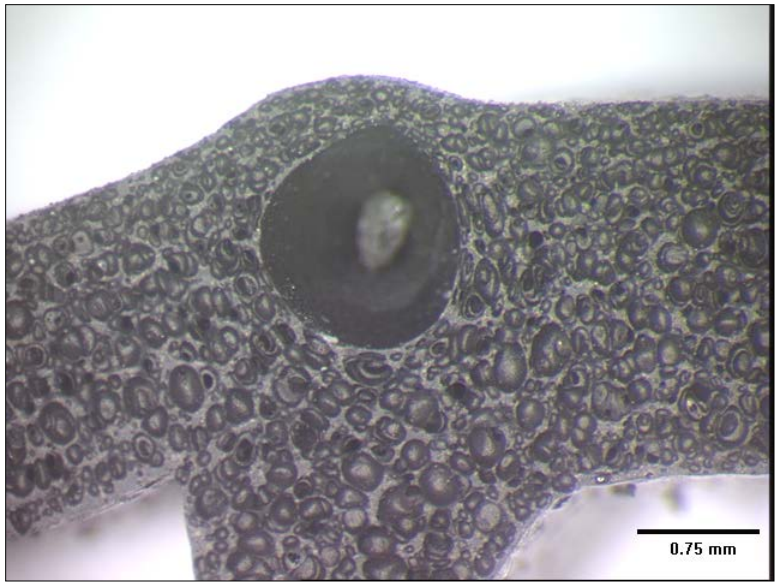
Vibrational Analysis of *n*-Alkanes

- methyl asymmetric C-H stretch
- methyl symmetric C-H stretch
- methylene asymmetric C-H stretch
- methylene symmetric C-H stretch
- methyl out-of-plane HCH deformation
- methylene and methyl in-plane HCH deformation
- methyl symmetric HCH deformation
- methylene wagging
- C-C stretching
- methyl terminal rocking
- CCC deformation
- methylene twisting-rocking
- methylene rocking-twisting

This is a fairly simple molecule.

Blister Defects in Rubber Door Trim

Problem: A local manufacturer was experiencing blister defects occurring in foam rubber pieces.

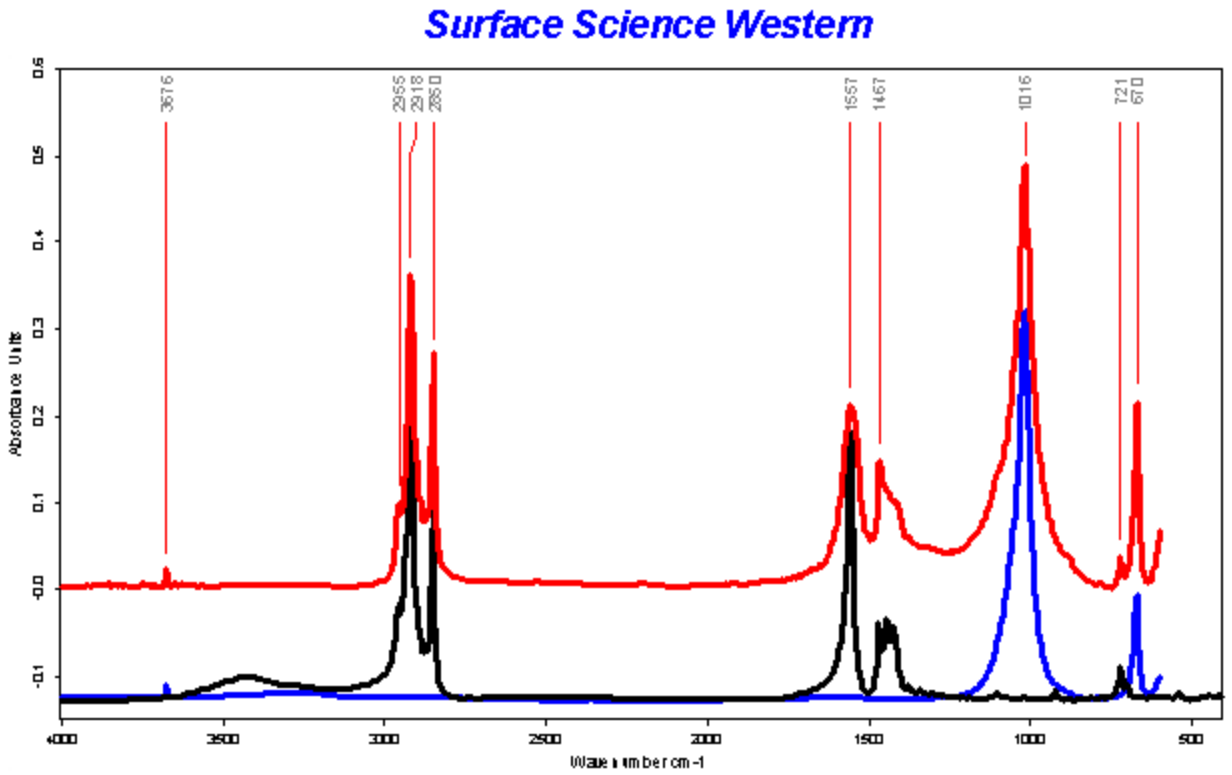


Approach: The defects were examined in plan view and in cross section. The cross sections showed the presence of a white particle in a void. Selected particles were then examined using energy dispersive X-ray (EDX) spectroscopy and Fourier transform infrared spectroscopy (FTIR).

Results: The EDX spectra show that the defect particles are mainly carbon, oxygen, silicon, calcium, and magnesium. Trace levels of potassium, sulphur, sodium, aluminium and zinc were also observed occasionally.

Blister Defects in Rubber Door Trim

A particle was also analysed by Fourier transform infrared spectroscopy (FTIR) using the microscope in transmission mode. The spectrum of the particle is shown below in red. A comparison with a match from our spectral library shows that the defect consists of two components, talc (blue) and sodium stearate (black).



Based on the FTIR and EDX analyses, the particle is a mixture of talc, sodium/calcium stearates and a small amount of calcium carbonate.

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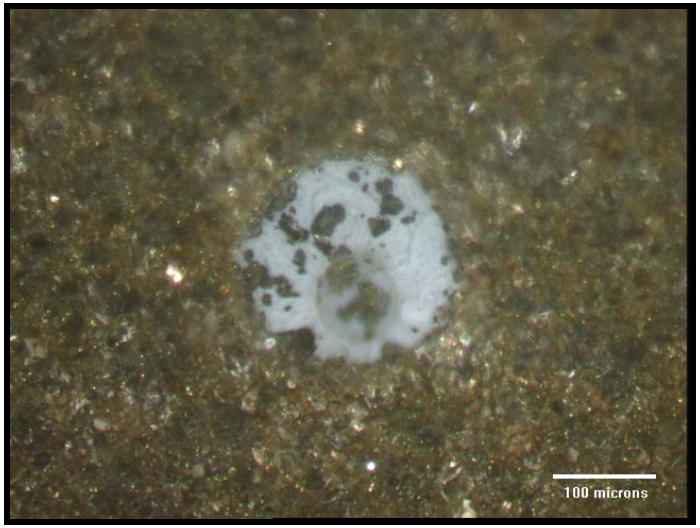
FTIR Analysis of Crater Defects

Problem: A client sent a fuel door exhibiting crater defects along with a test panel with potential contaminants (one of which was craters created using a Polysporin® reference). We were asked to examine and identify the defect material in the craters.



Approach: Multiple crater defects from the fuel door were examined using optical microscopy. The crater defects appear to have a “white” centre when viewed with polarized light. The white centres are associated with a “splash” pattern. Various areas in and around the crater centres were analysed using Fourier transform infrared (FTIR) spectroscopy and energy dispersive X-ray (EDX) analysis.

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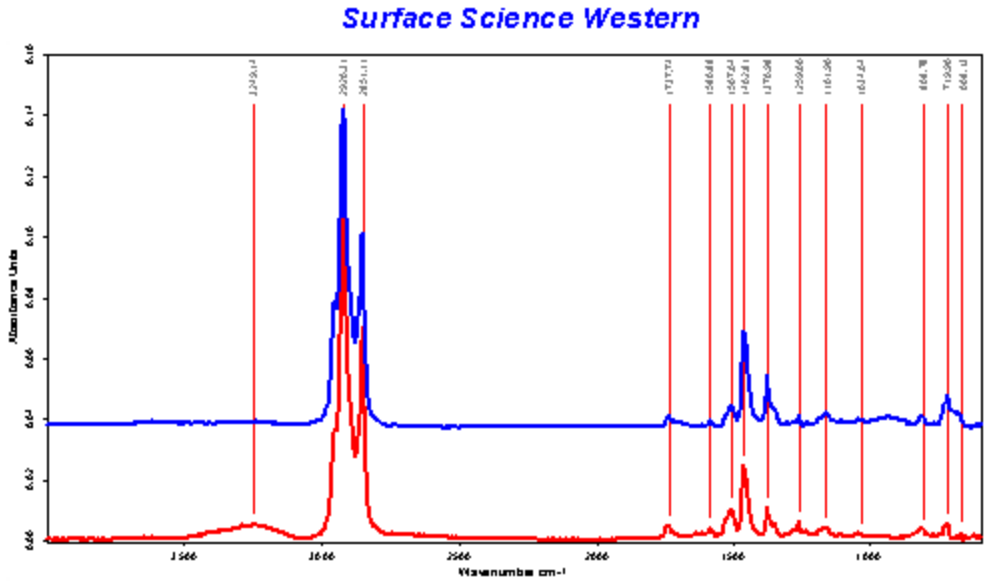
FTIR Analysis of Crater Defects

Results: The defect craters and reference samples were analysed by FTIR spectroscopy in micro attenuated total reflection mode (micro ATR). The most obvious material seen in the defects was a liquid which oozed on FTIR analysis. The FTIR spectrum of the material oozing out of one of the defects was consistent with a hydrocarbon. The material in the Polysporin reference sample, a hydrocarbon, was found to be a match to the liquid material found in the centre of the defects by FTIR.



The craters were also analysed by SEM/EDX. The EDX analysis of the reference area and the crater centre showed only the presence of carbon and oxygen.

Based on the FTIR results, the defect material inside the craters is a match to the defect material in the craters of the Polysporin® reference.

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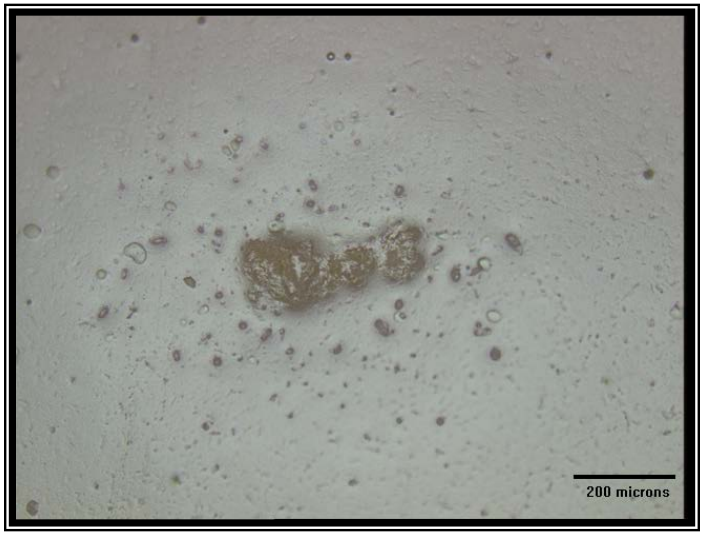
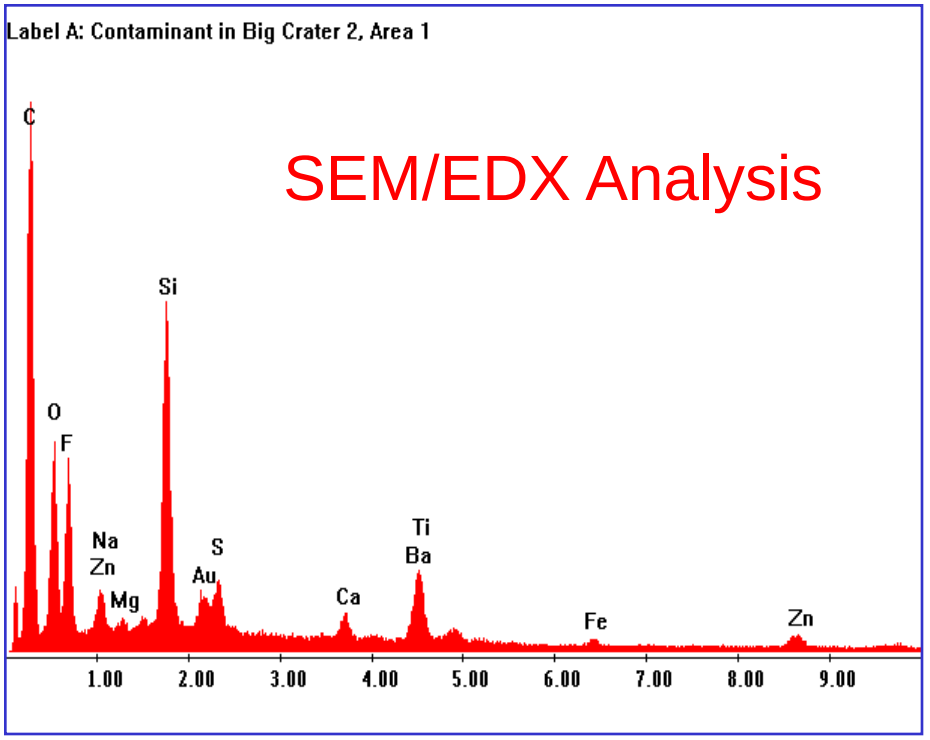
Micro FTIR-ATR Analysis of Crater Defect in Painted Panel



Optical image of crater defect in painted panel



Sample	Elements Detected (Atomic Percent)												
	C	O	F	Na	Mg	Al	Si	S	Ca	Ba	Ti	Fe	Zn
Reference area	79	16	–	–	–	0.2	0.9	0.7	0.5	0.6	1.5	–	0.4
Contaminant area	72	14	7.7	0.3	0.1	–	3.3	0.5	0.3	0.2	1	0.2	0.7

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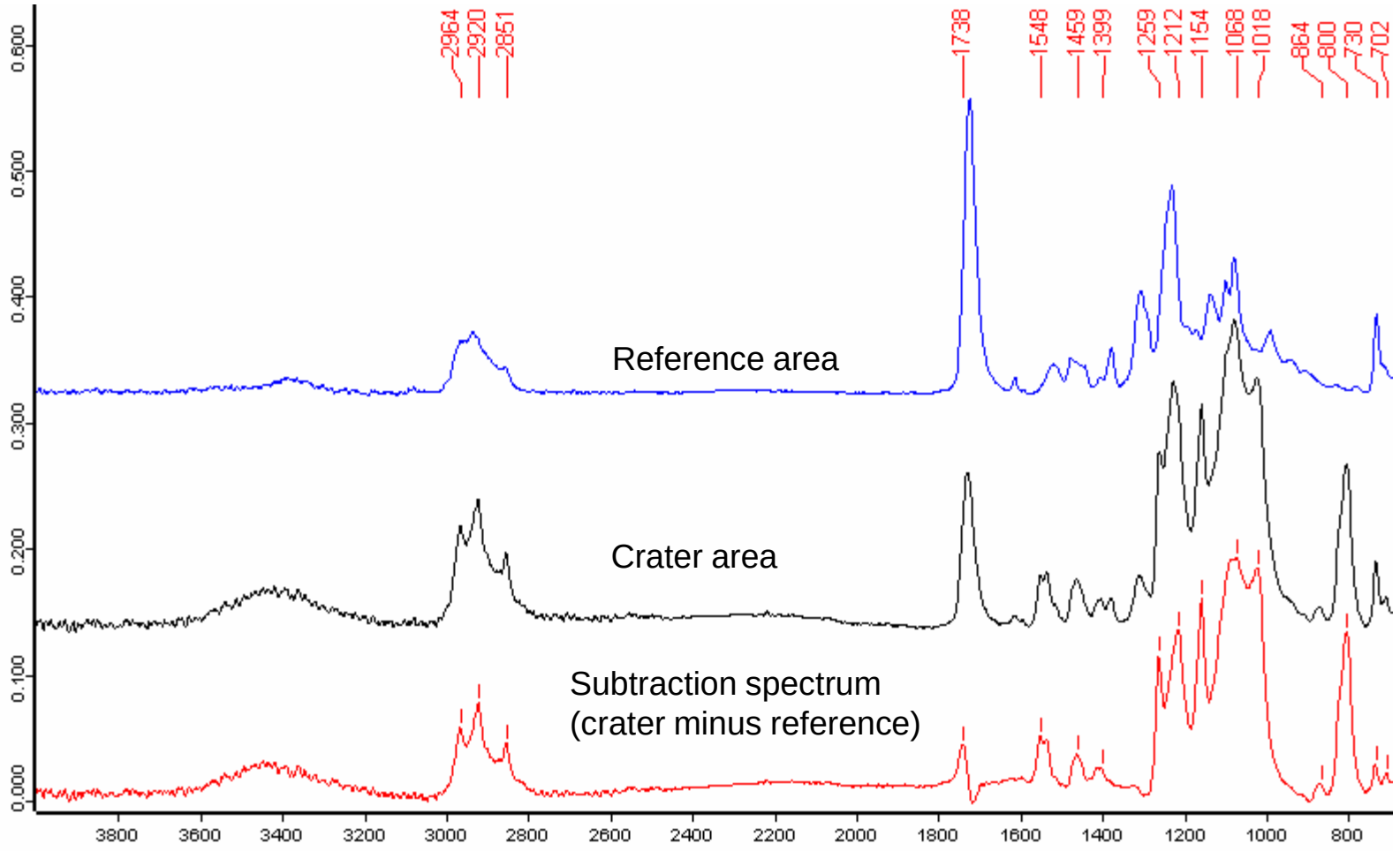
FTIR-ATR Spectra from the Crater and the Surrounding Reference Area



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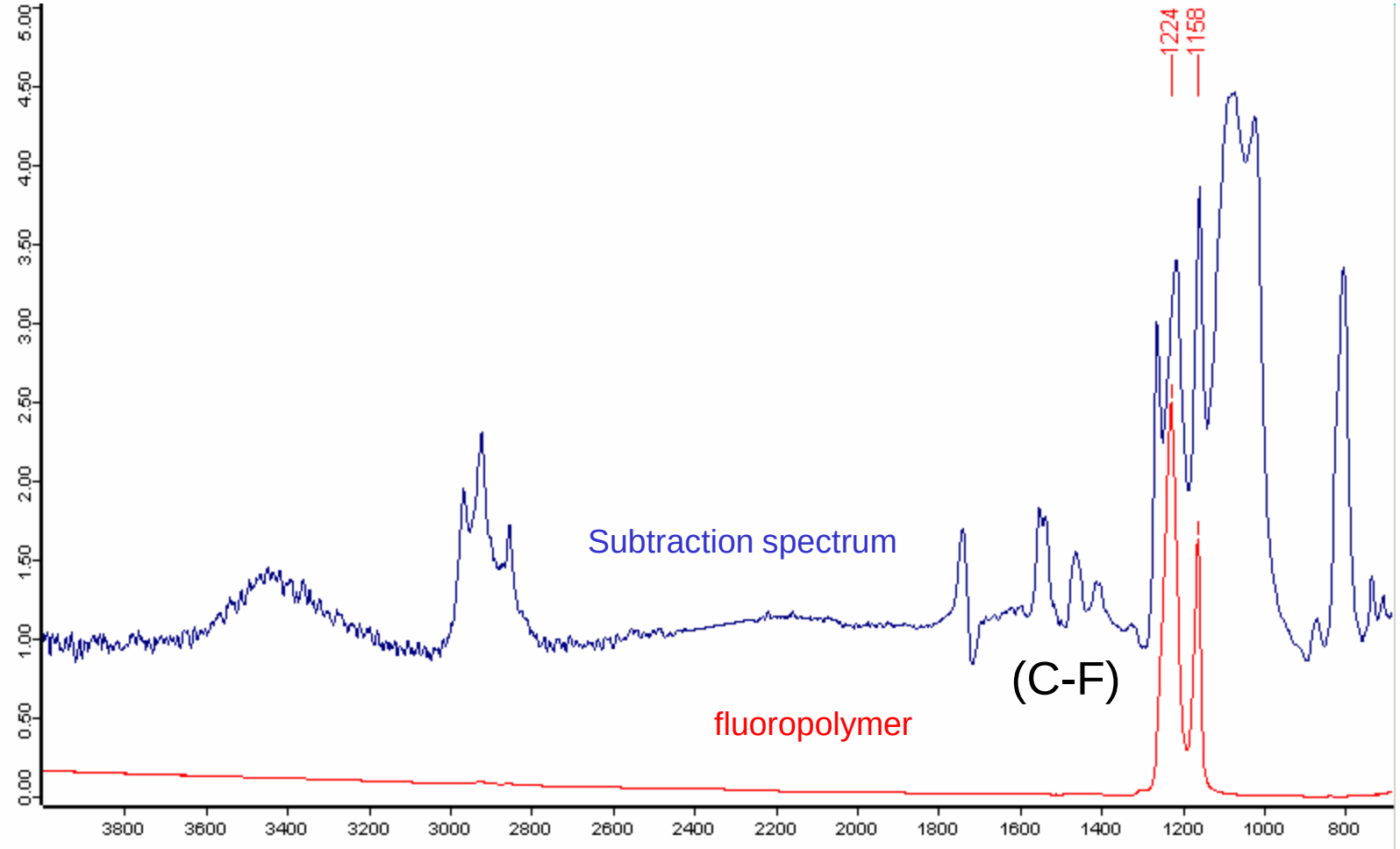
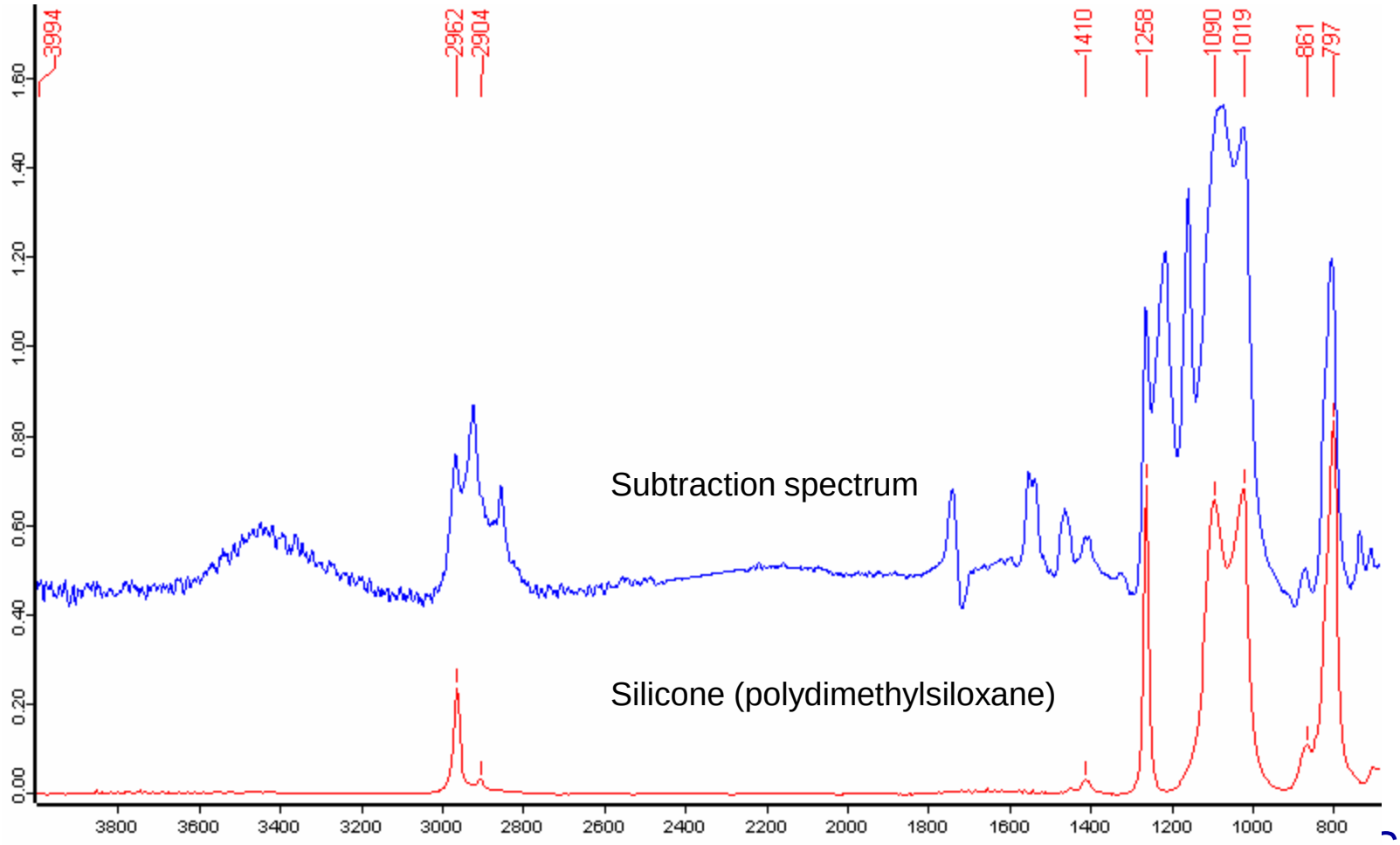
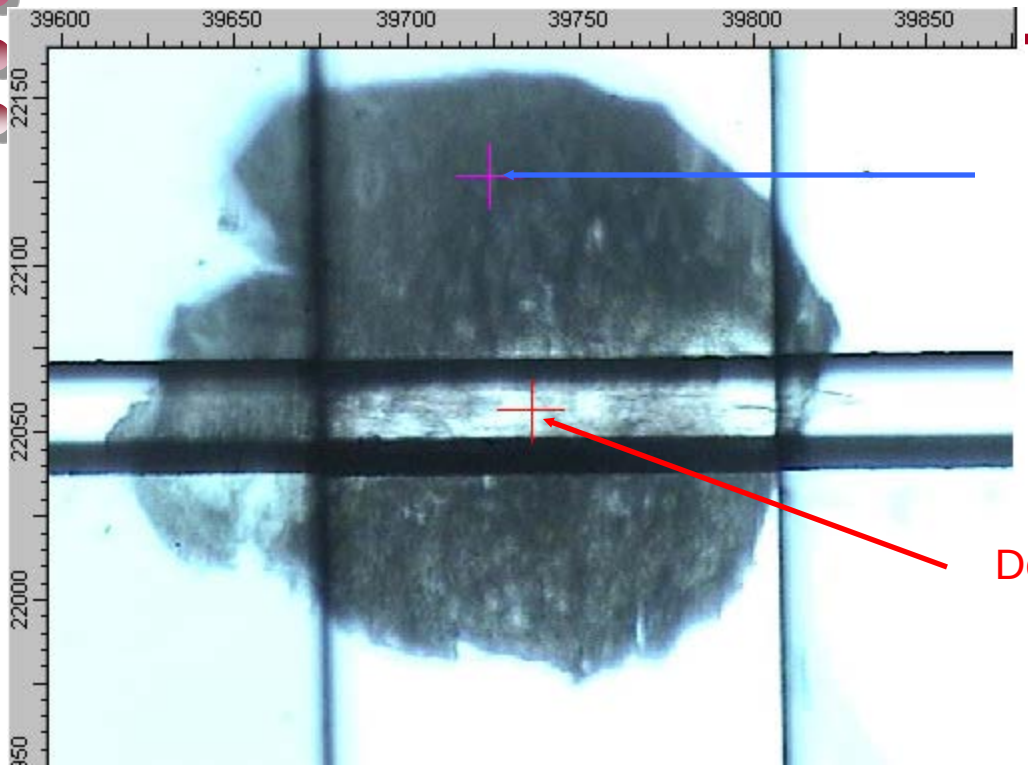
- Our electronic database was searched for a match to the spectrum from the crater: no match was found. The contaminant material is most likely a mixture. Peaks at 1224 and 1153 cm^{-1} were matched with those in a reference spectrum of a fluoropolymer.



Silicones are known cratering agents. Peaks at 1260, 1090, 1019, 861 and 797 cm^{-1} were matched with those in a reference spectrum of a silicone (polydimethylsiloxane (PDMS)).



Microscopic FTIR Analysis of a Defect in a Paint Coating

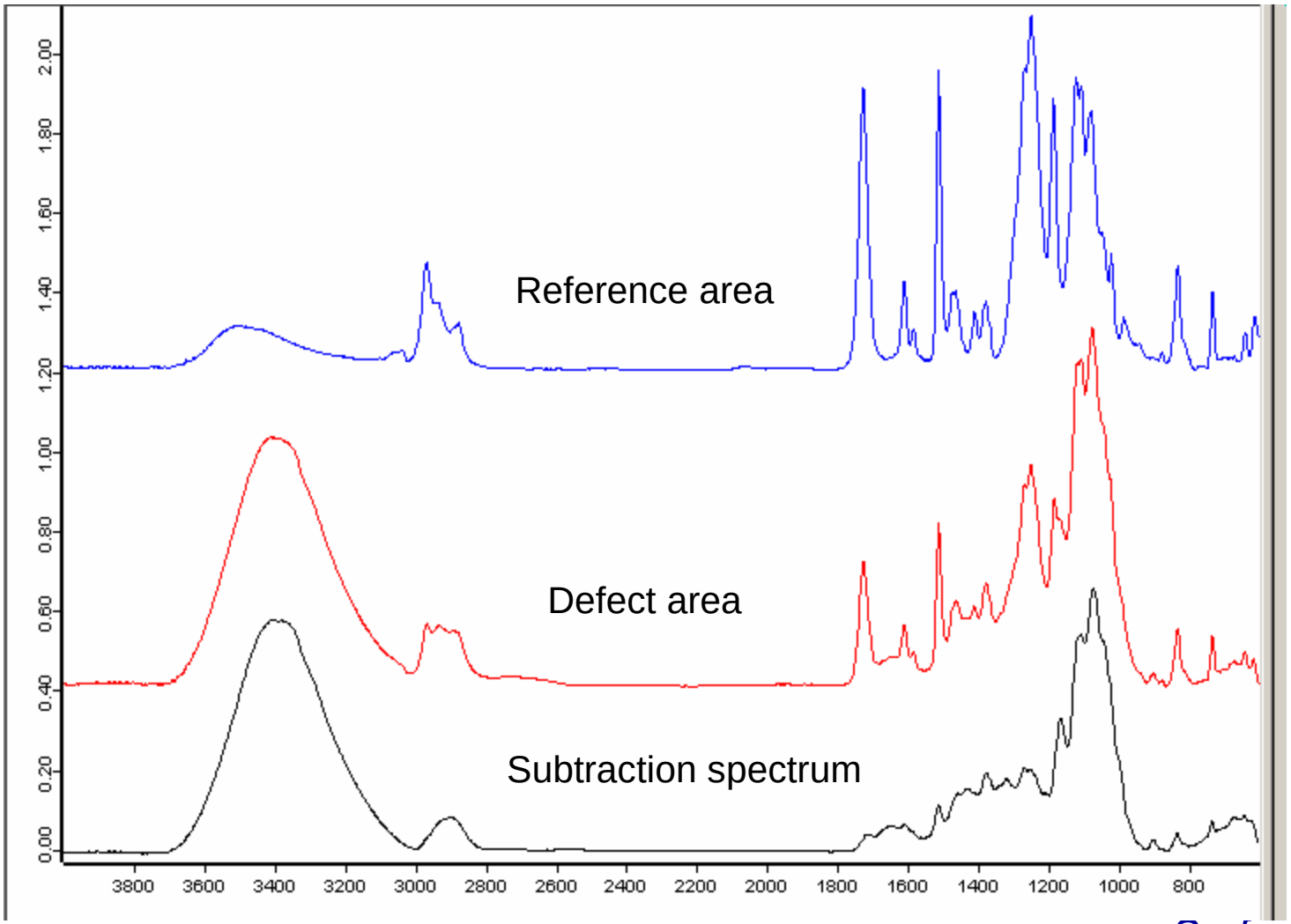


Reference area

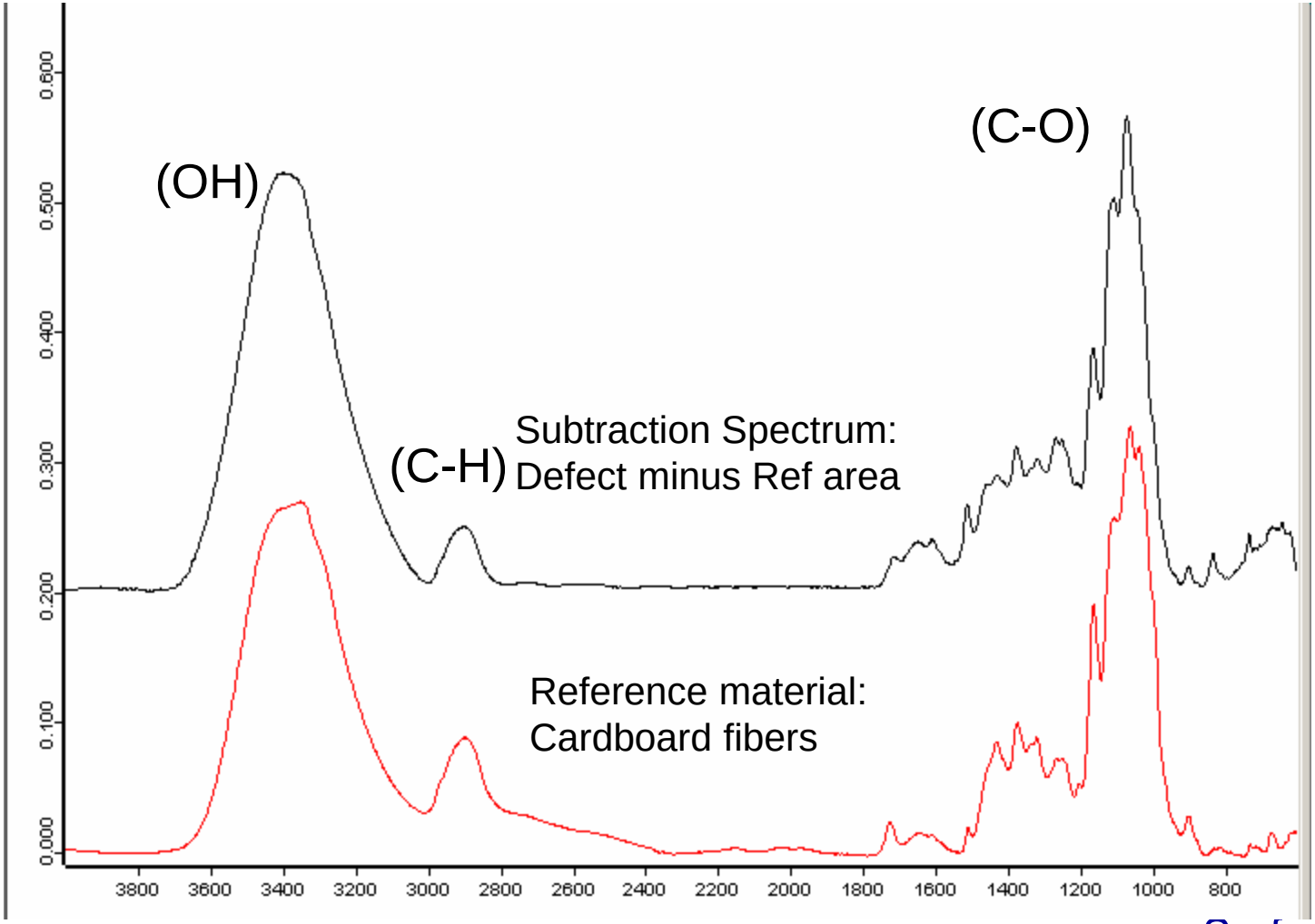
Defect area

Figure showing an optical image of the cross-section of paint coating with defect. FTIR spectra of the defect area and a reference area were obtained in transmission mode through one of the diamond windows, using the microscope attachment. An aperture size of approximately 150 x 50 microns was used for the analysis.

Defect Area, Reference Area and Subtraction (Defect – Reference) Spectra



FTIR analysis of a defect in a paint coating revealed that the defect is a cellulose-based material. Cardboard was identified as a possible source of these cellulose-based fibers.



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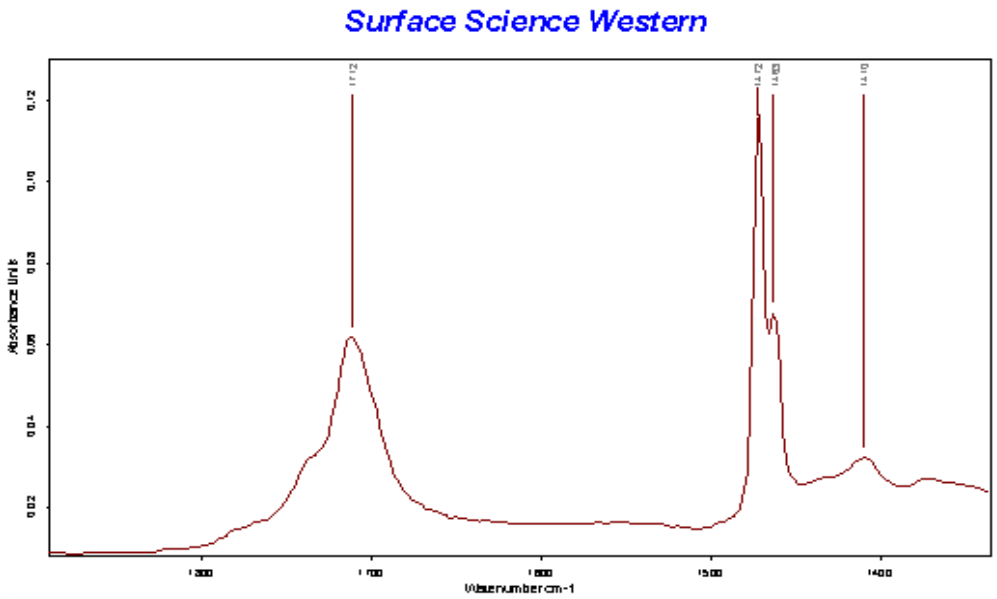
ENVIRONMENTAL DEGRADATION OF POLYMER PIPING

Environmental degradation of polyolefin piping materials (polyethylene, polypropylene and polybutene, for example) has a significant impact on many water delivery systems. We have investigated oxidative degradation in a number of polymer pipes that have been in use in the distribution of potable and non-potable water.



FTIR Analysis

The broader peak centred near 1712 cm^{-1} arises from the carbonyl groups generated in the oxidative degradation of the pipe. The pair of peaks at 1473 and 1462 cm^{-1} arise from the scissoring mode of the CH_2 groups in the polymer which are relatively unaffected by the degradation. A ratio of the area under the peak centred near 1712 cm^{-1} versus the area under the peaks at 1462 and 1473 cm^{-1} is calculated to give a carbonyl ratio which reflects the degree of oxidative degradation in the polymer.

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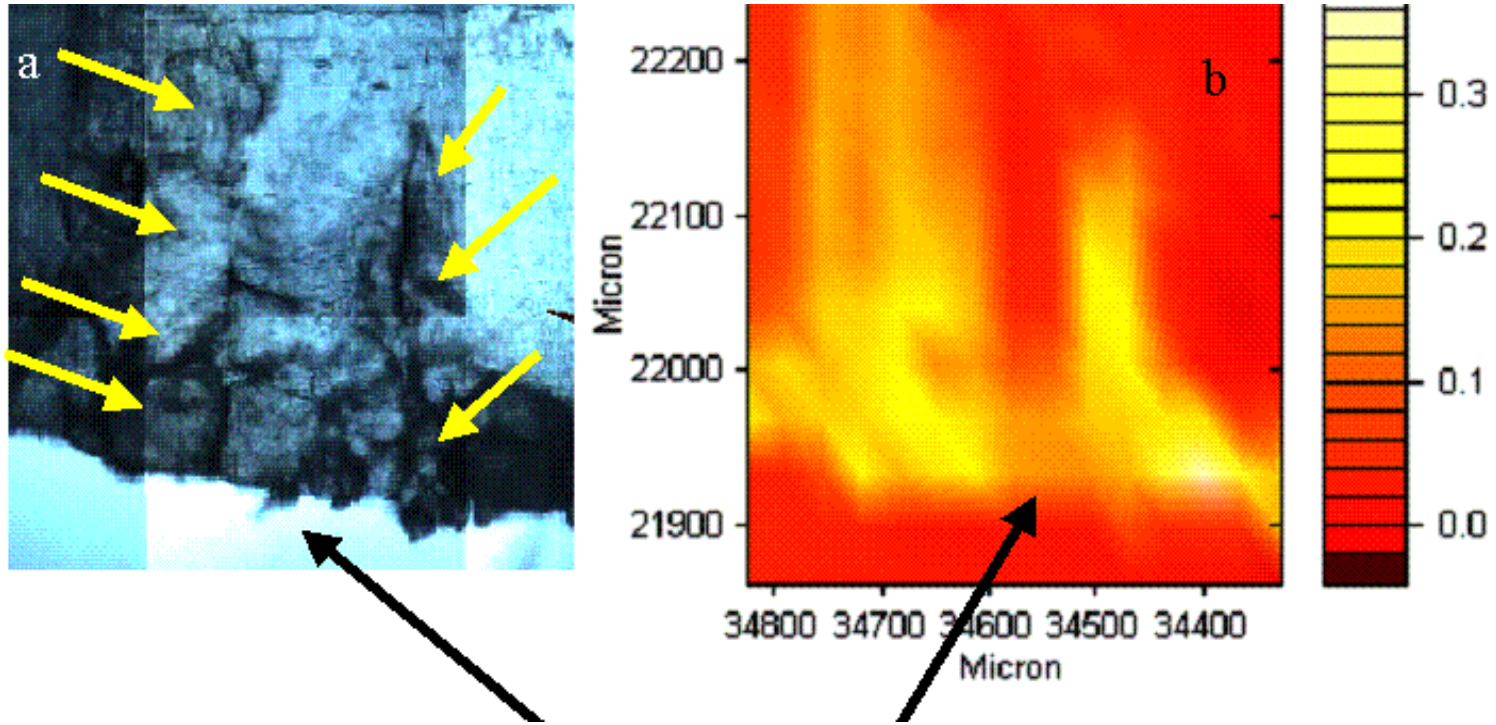
ENVIRONMENTAL DEGRADATION OF POLYMER PIPING

Mapping of thin sections of materials by FTIR can also be accomplished using the microscope attachment in transmission mode. The correlation between the crack area and the increase in the absorbance in the carbonyl region can clearly be distinguished using this technique.

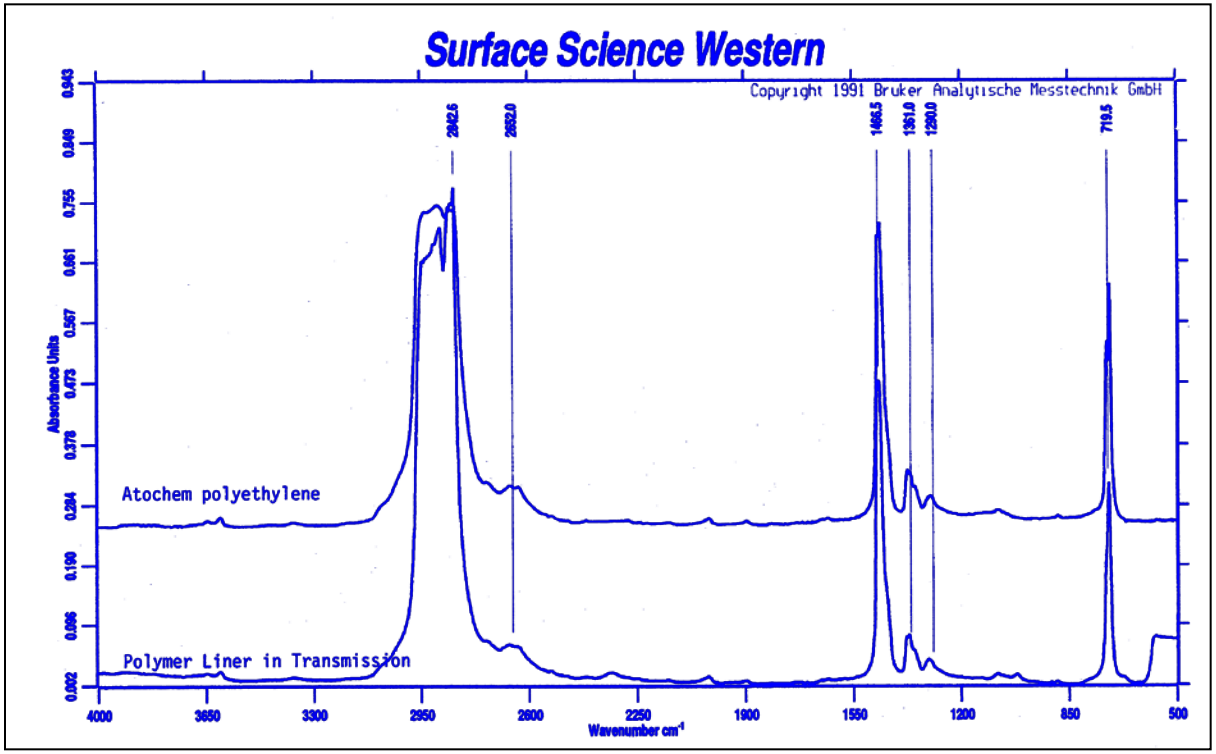


Optical image of the cross section of the pipe showing two cracks in image A and the corresponding integrated intensity image of the carbonyl region in image B.

ANALYSIS OF POLYMER FILMS BY FTIR-ATR

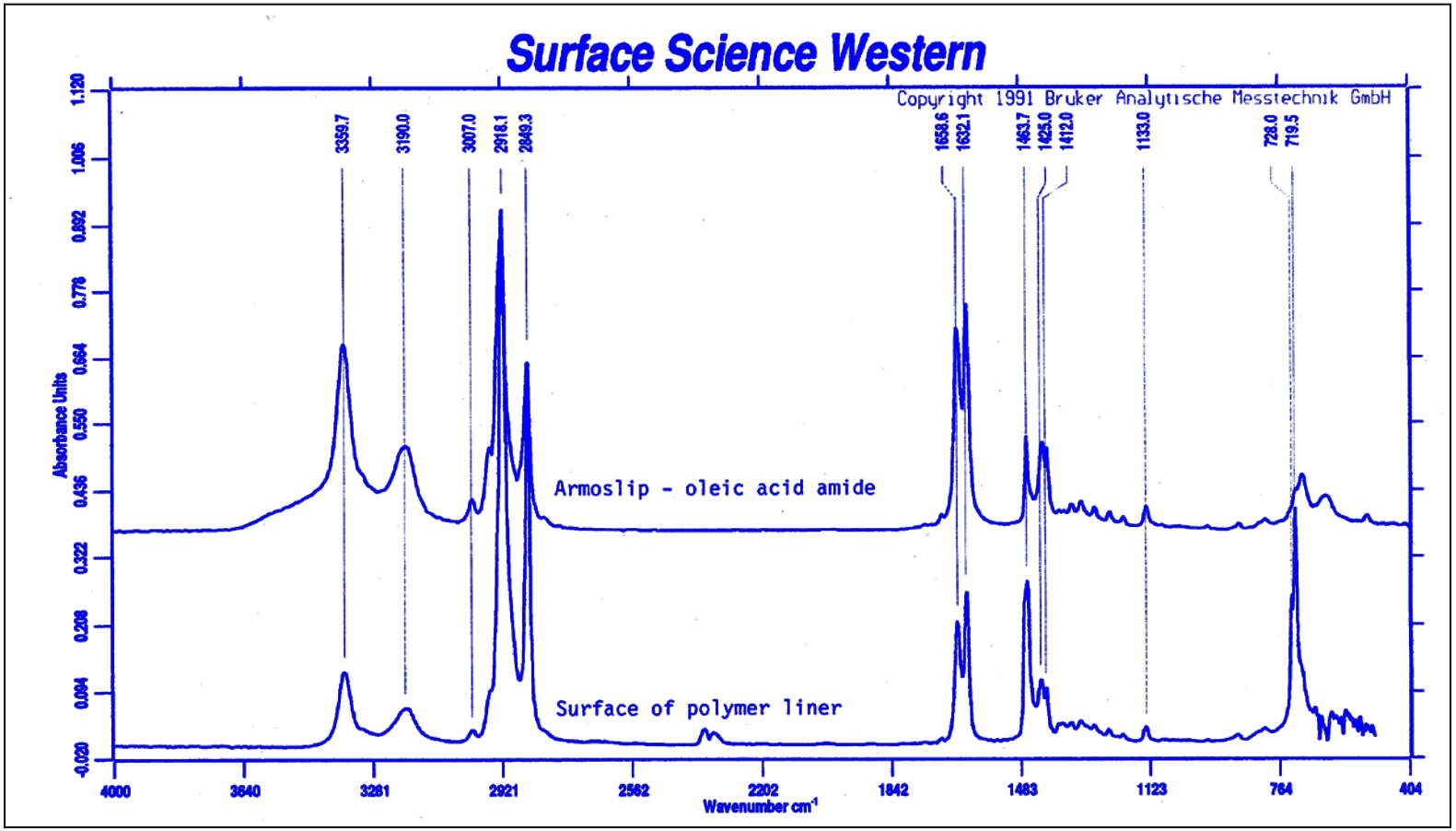
PROBLEM: The client has some doubts about a polymer liner that they received. It is not behaving the same as previous liners. They wanted to know if there was anything different about this liner. SEM/EDX shows the presence of only carbon and oxygen on the two surfaces.

- The liner is analyzed in transmission mode to determine the polymer used. The two surfaces are then analyzed by FTIR-ATR.



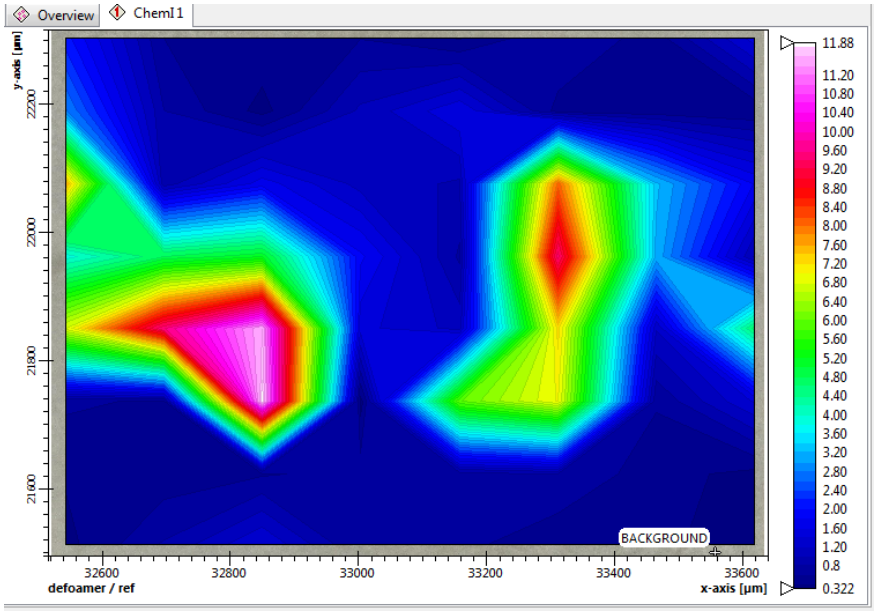
The FTIR spectrum of the bulk polymer in transmission mode is consistent with polyethylene.

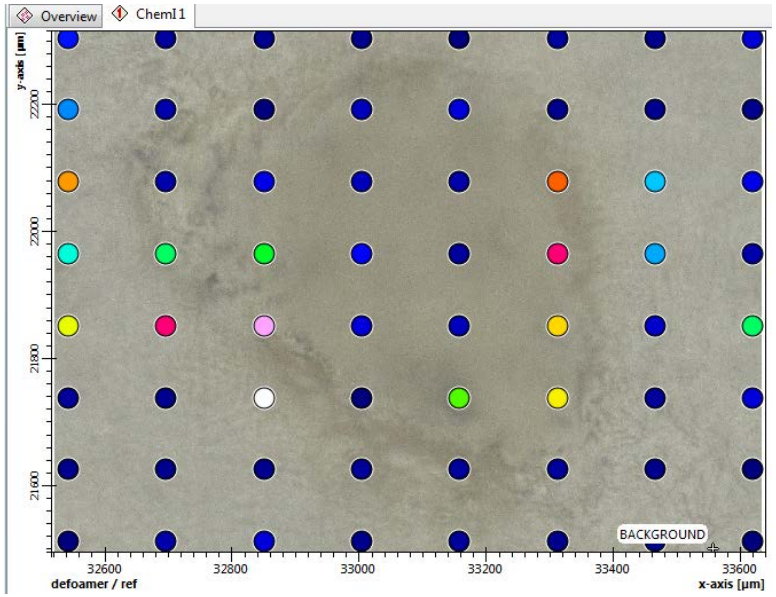
ANALYSIS OF POLYMER FILMS BY FTIR-ATR



FTIR-ATR shows one side of the sample to have a layer of long-chained amide present. These long-chained amides, erucamide and oleic acid amide, are often used as slip agents for various polymer films and can interfere with adhesion.

ANALYSIS OF CRATERS BY MICRO-ATR MAPPING





A paint crater was analysed using micro-ATR mapping on the FTIR microscope. Examination of the maps showed the presence of a foreign material on the edge of the crater.

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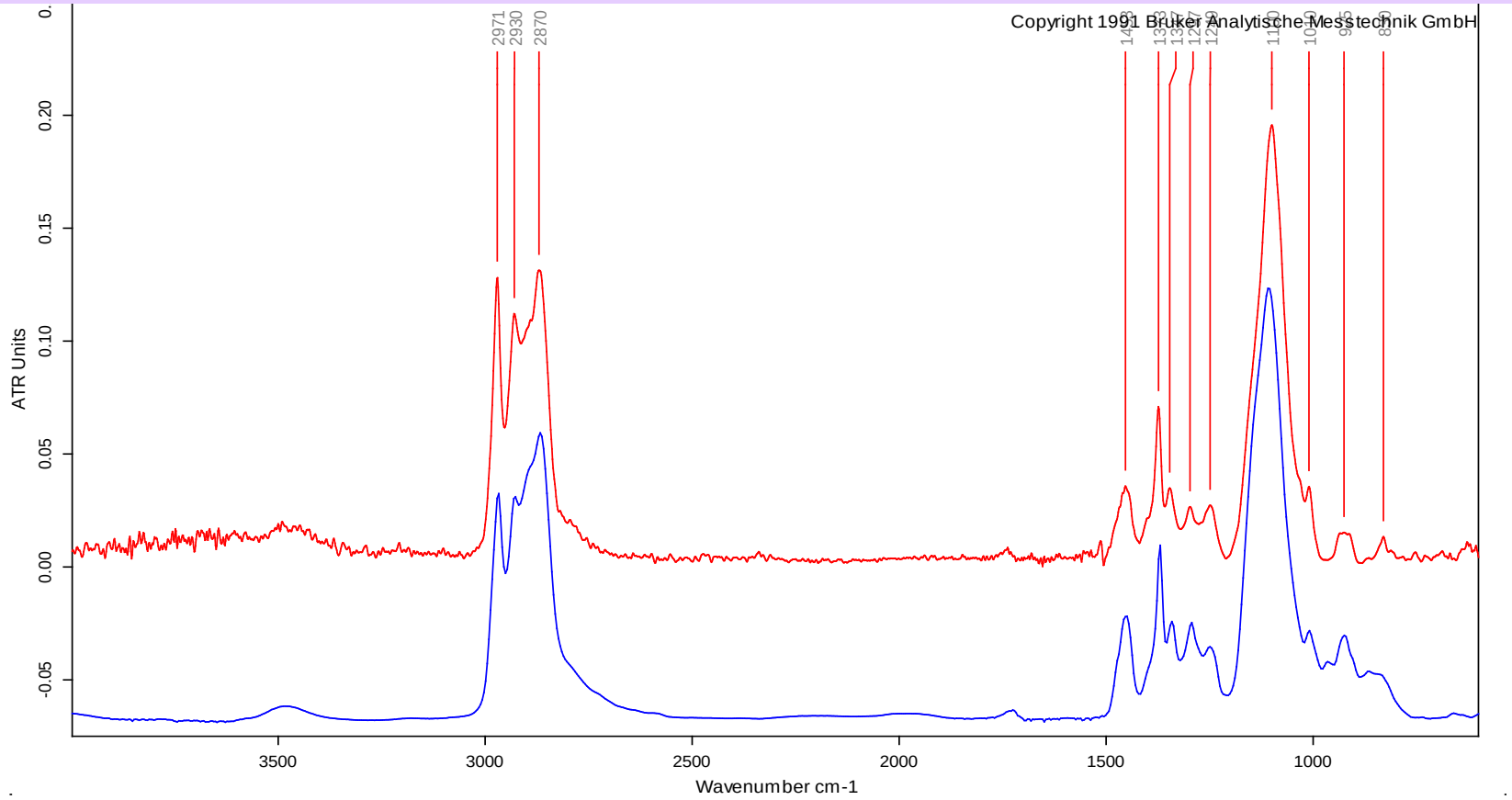
ANALYSIS OF CRATERS BY MICRO-ATR MAPPING



12016 NIS AREA 1 MINUS AREA 3

DEFOAMER FOR WATERBASED SYSTEMS

Filename: AREA1MINUSAREA3_0.100
Date : 3/24/2016
Resolution : 4, # of scans : 8

Technique : HYPERION 2000_20X ATR OBJECTIVE
Experiment : Hyperion 2000_ATR_ATR.XPM
User : Administrator

The spectrum of the foreign material is consistent with a defoamer.

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Advantages of Raman Spectroscopy

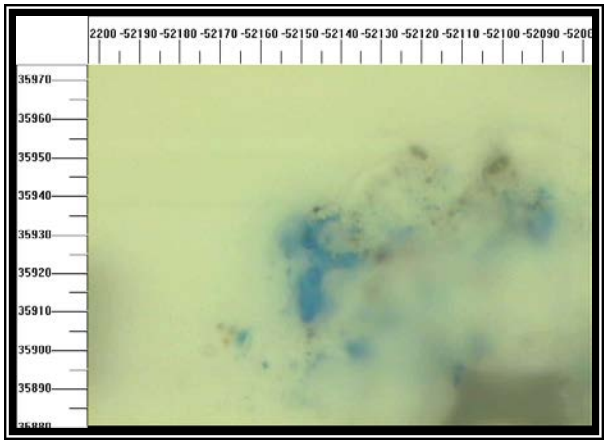
- Because Raman spectroscopy is a scattering process, samples of any size or shape can be examined.
- Very small amounts of material can be studied down to microscopic levels - 1 micron.
- Fiber optics can be used for remote sensing.
- Aqueous samples can be studied.
- The region from 80-500 cm^{-1} can be studied with no changes on the same instrument.

Typical Applications of Raman

- Determination of various carbon forms e.g. diamond vs. diamond-like carbon vs. graphite vs. amorphous carbon.
- In situ aqueous analysis.
- Identification of inorganic oxides, sulfates, phosphates and mineral forms.
- Backbone analysis of polymers.

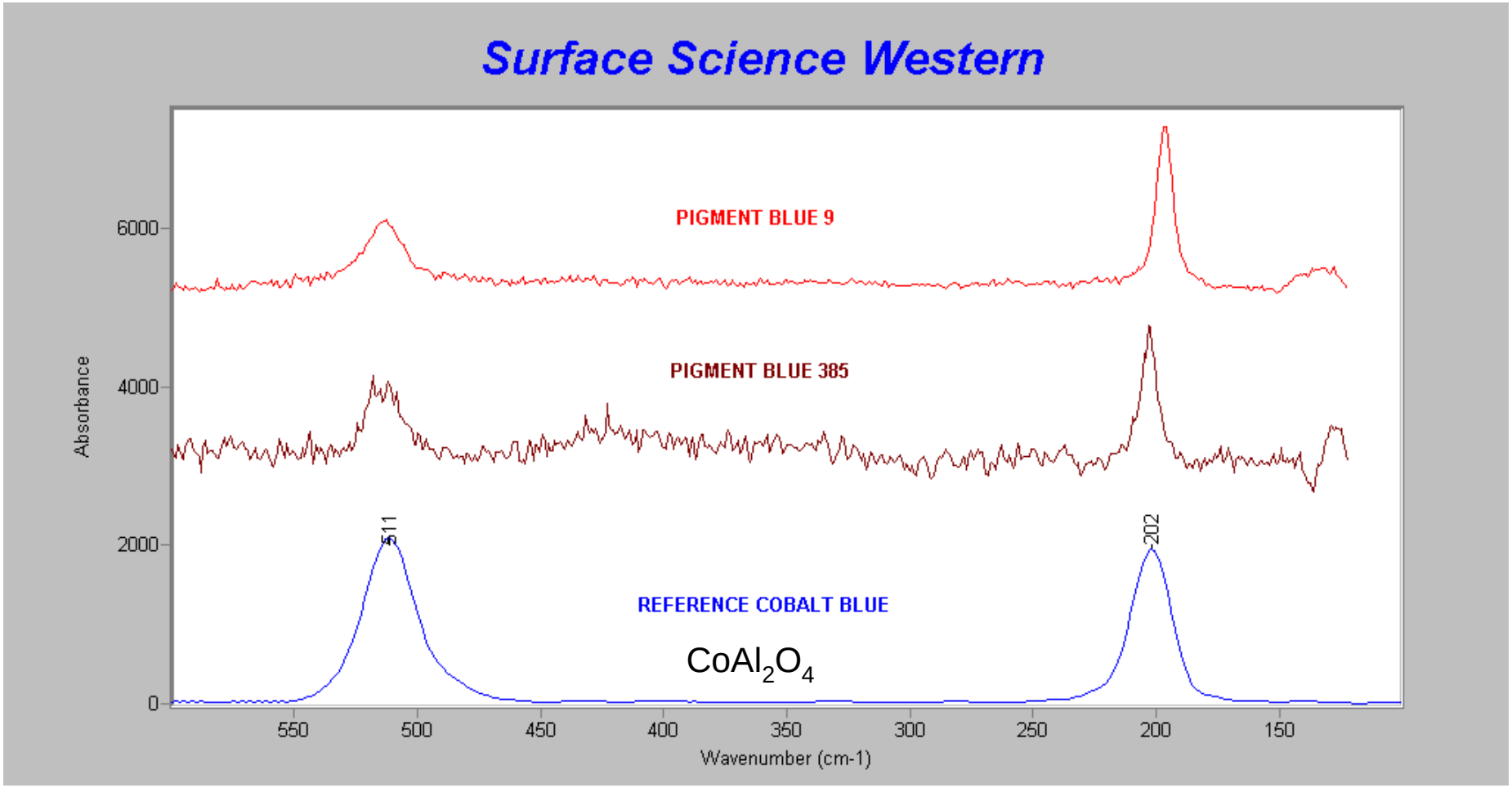
CONTAMINATING BLUE STREAKS IN PAINTED PANELS

PROBLEM: The client formulates paint and in generating his test panels before shipping the paint, he notices that there are blue streaks in the test panels. The paint is white and does not contain a blue pigment. He would like to know what is causing the blue streaks.

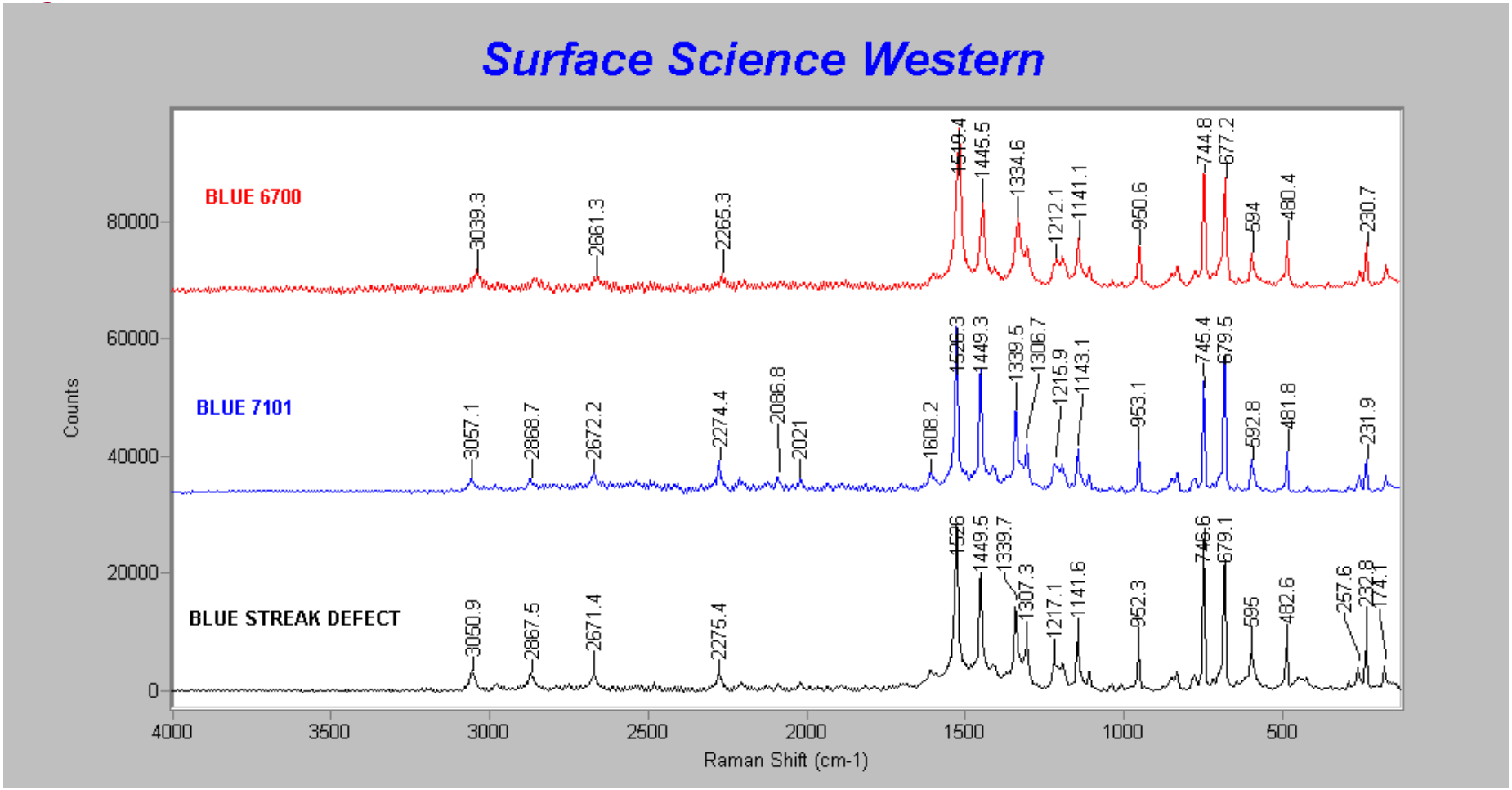


APPROACH: The blue streak was analyzed by FTIR-ATR but the results were inconclusive. Because of the intense colour of the streak, the area was analyzed by Raman spectroscopy and a sharp, well-defined spectrum collected. The spectrum was similar to a nickel phthalocyanine spectrum in our library but was not an exact match. The client supplied 4 blue pigments which were present in his plant for us to determine which pigment matched the streak.

The initial pigments were based on cobalt blue and did not match the Raman spectrum of the streak.



The next set of pigments were both copper phthalocyanines, one in the epsilon form and one in the beta form.



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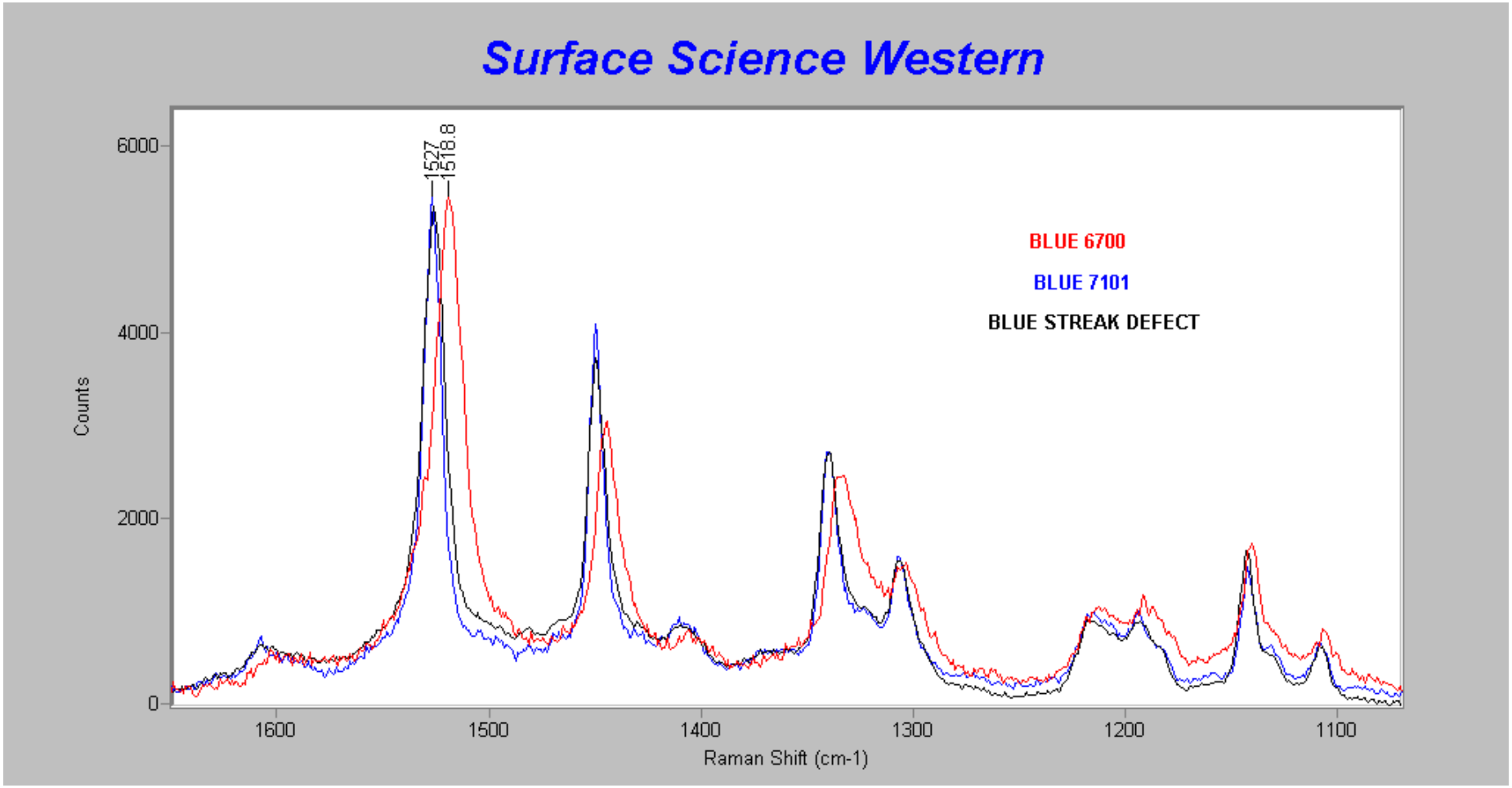
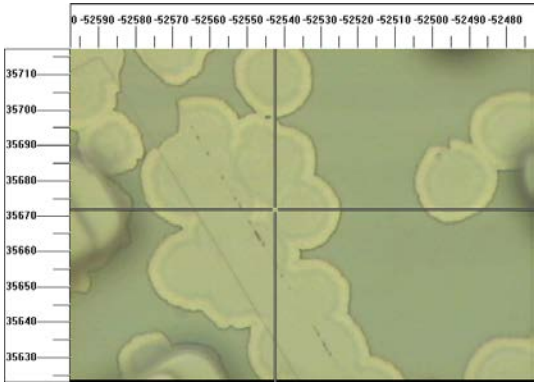
The blue streak most closely matched the Blue 7101, copper phthalocyanine in the beta form



DEFECTS FORMING ON SELENIUM COATING WITH TIME

PROBLEM: The client was noticing the formation of a crystalline material on its selenium coating with time. They requested identification of the crystalline material. EDX analysis showed only the presence of selenium.



APPROACH: The various areas on the sample were analyzed by Raman spectroscopy. The different forms of elemental selenium have very strong Raman signals.

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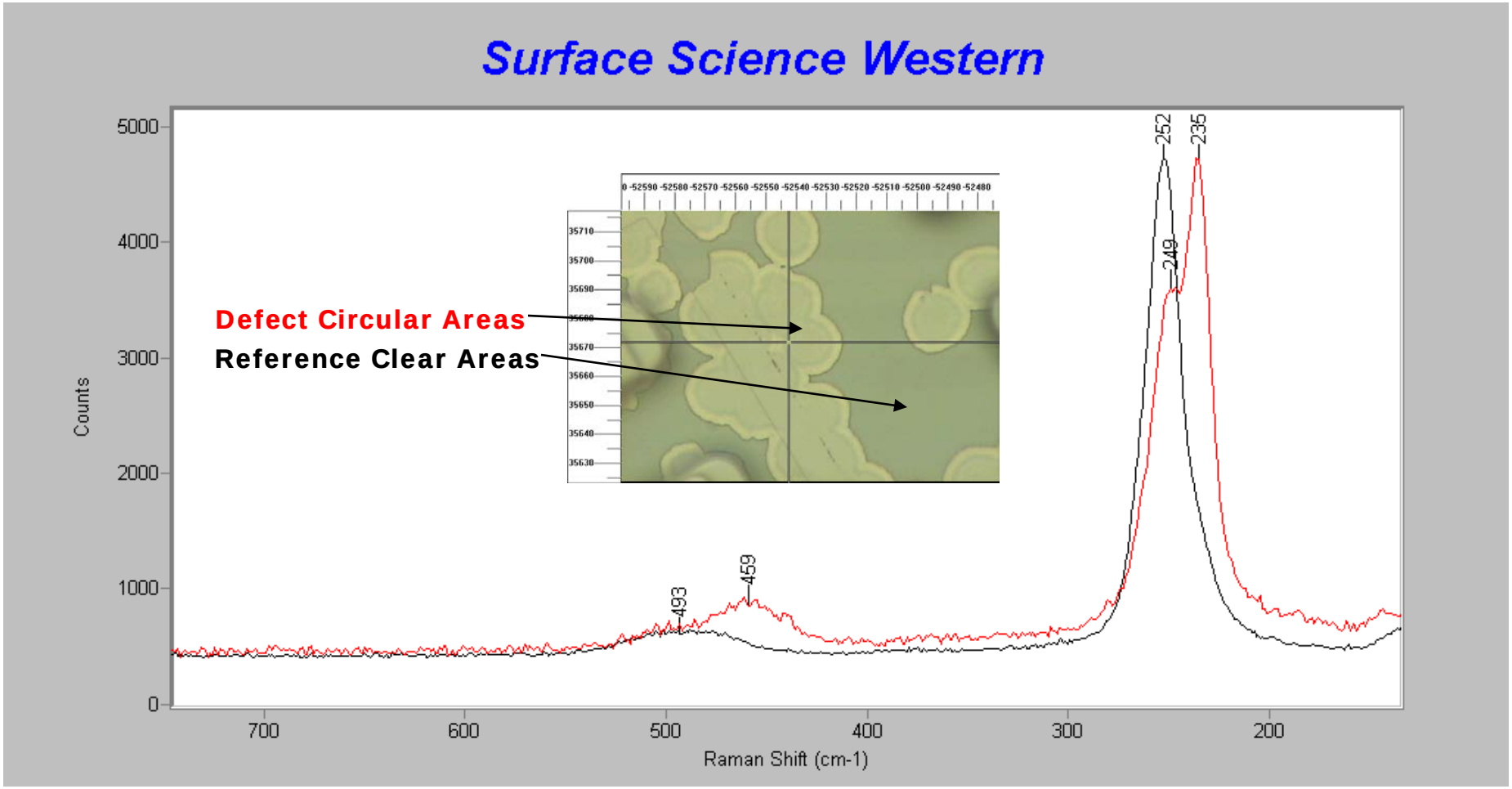
The spectrum of the selenium varied with the location analysed. A representative area was mapped.



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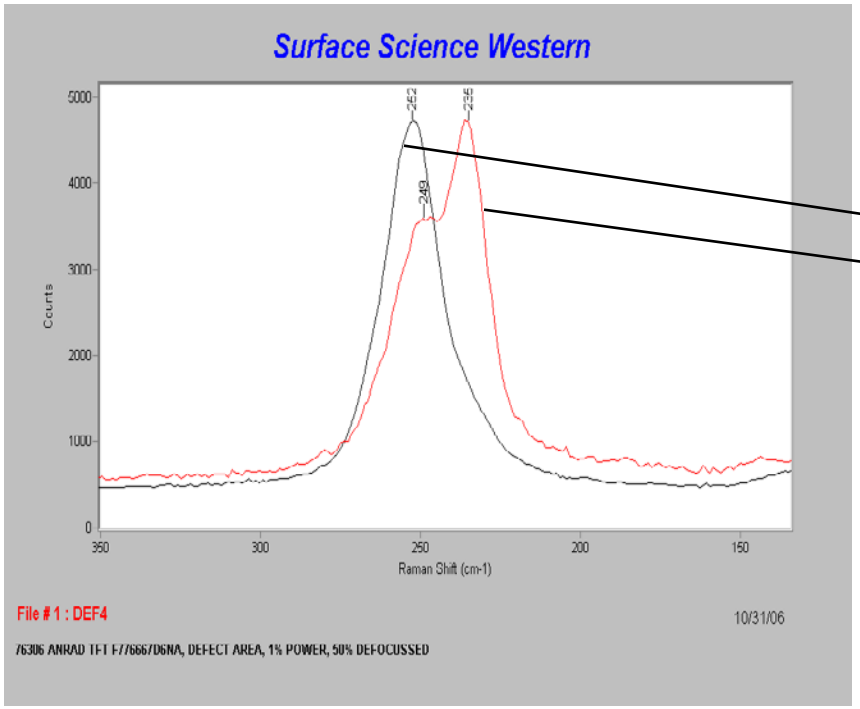
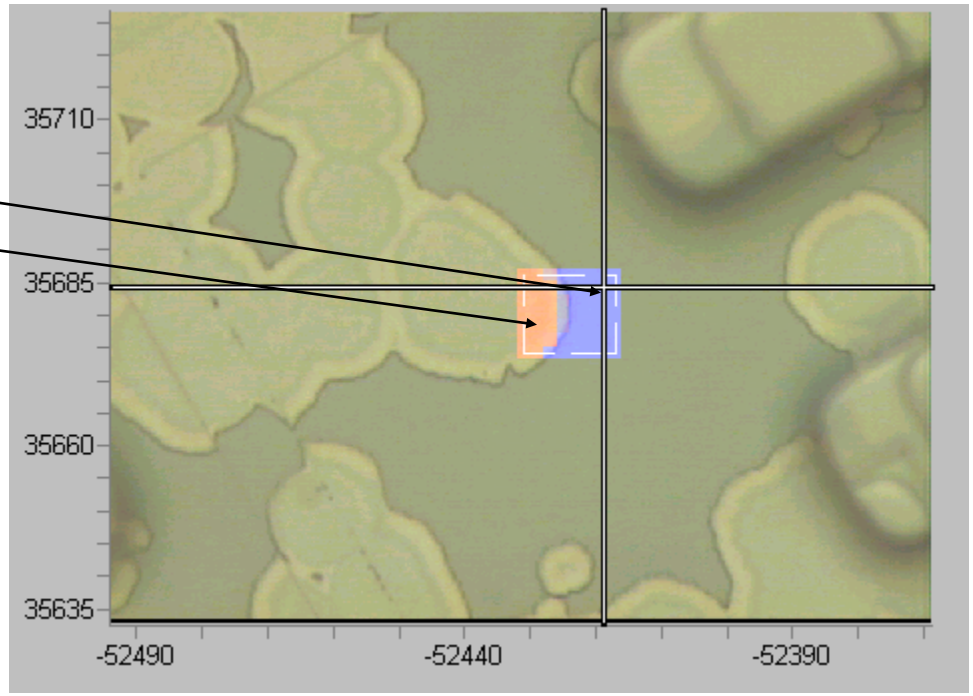
According to various references, the shift in the peak location is linked to the form of the selenium in the sample. The band at 252 cm^{-1} arises from vibrations in the Se_8 rings while the band at 235 cm^{-1} arises from trigonal selenium.





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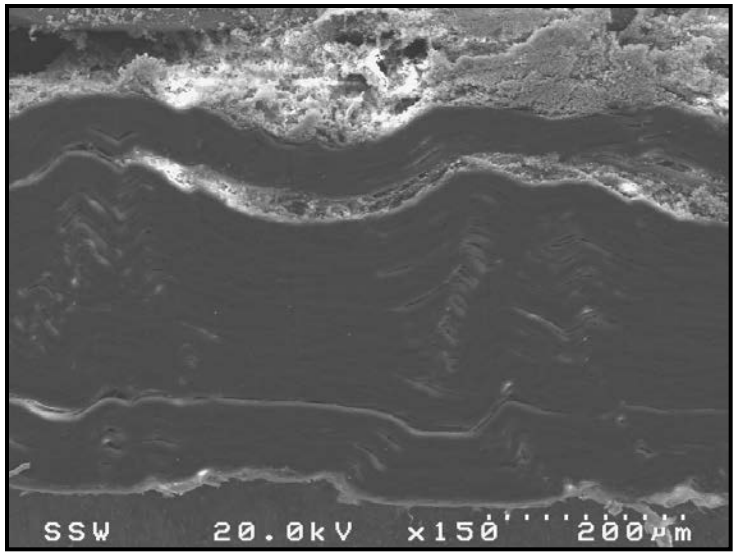
SPLITTING OF A POLYPROPYLENE MEMBRANE

PROBLEM: A section of a large polypropylene membrane was experiencing delamination and failure in use. The client wanted to know if the cause of the failure was premature oxidative degradation of the polymer.



APPROACH: The typical approach for this type of analysis is SEM/EDX analysis to determine the elemental composition and FTIR to examine the oxidative degradation. In this case, the sample was significantly contaminated and the FTIR analysis did not support the theory of oxidative degradation. The sample was examined by Raman spectroscopy because of the obvious layered structure.

In a reference area of the part which was not experiencing failure, the sample was examined both parallel and perpendicular to the incident laser beam to determine if there was any alignment of the polymer strands. There was no orientation.

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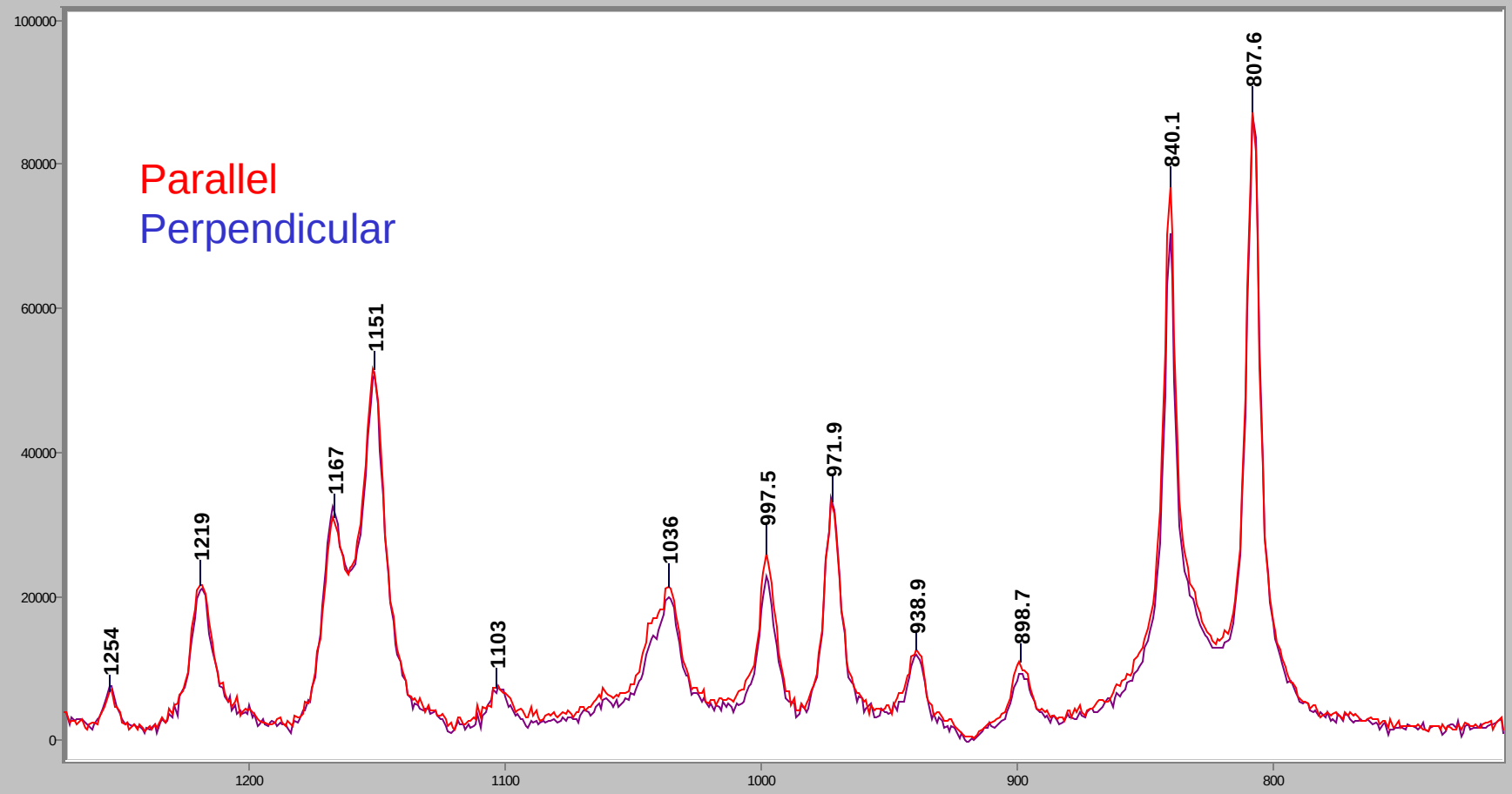

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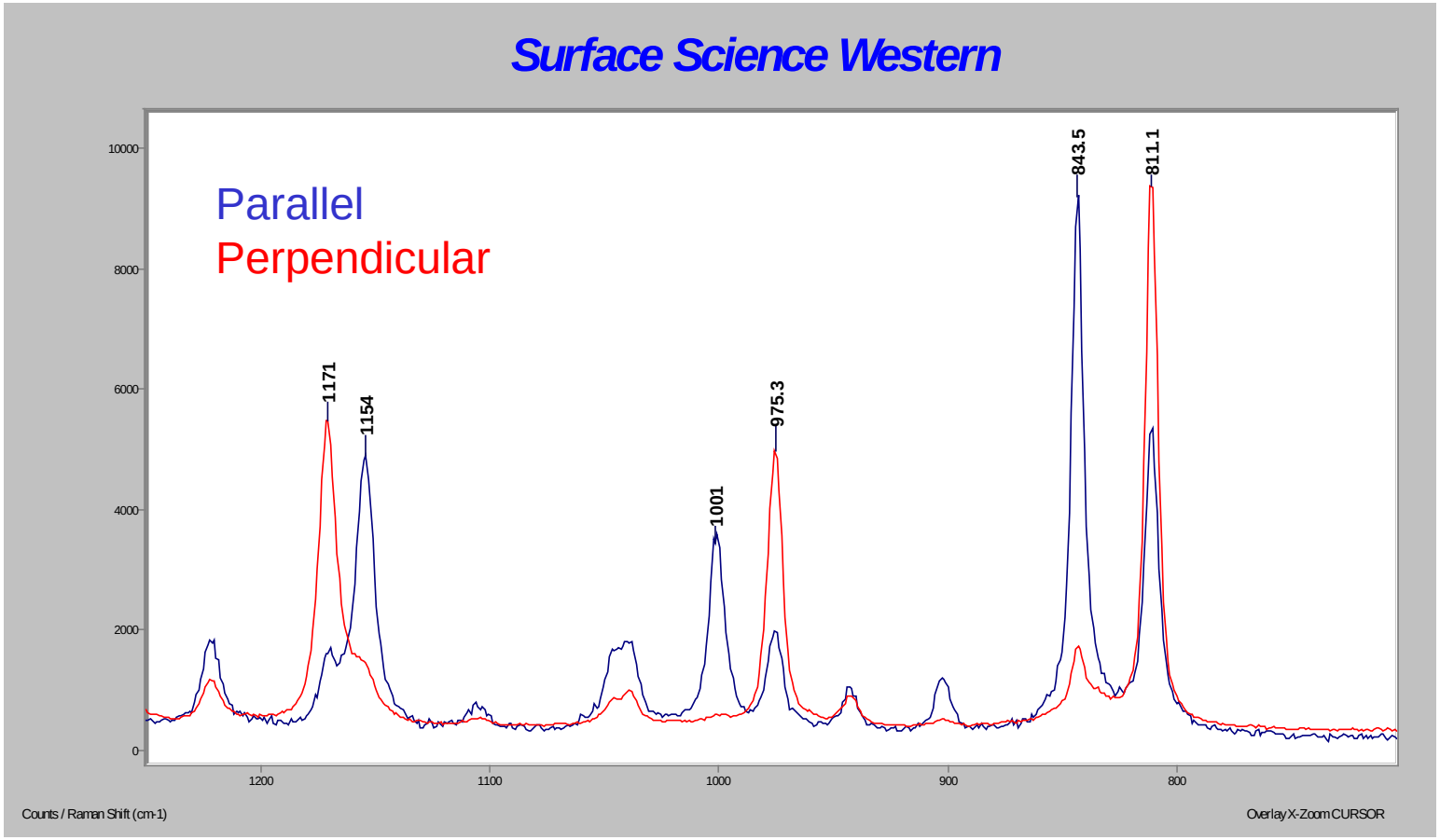
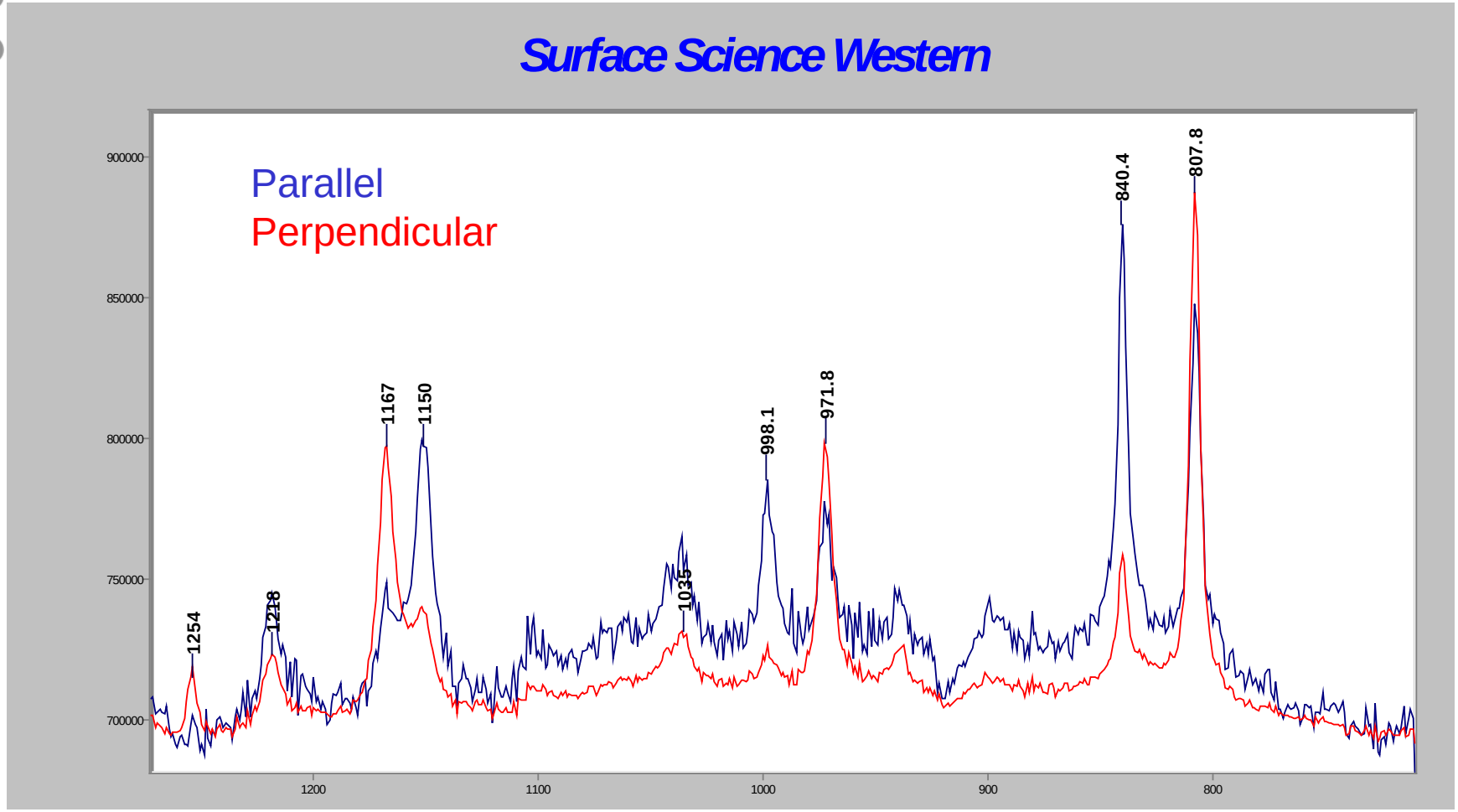
For comparison, the Raman spectra of near uniaxially oriented polypropylene collected parallel and perpendicular to the laser beam are shown.



The Raman spectra of the delaminated portion of the membrane was analysed in a similar manner showing significant alignment of the polymer chains, leading to the delamination and failure of the part.



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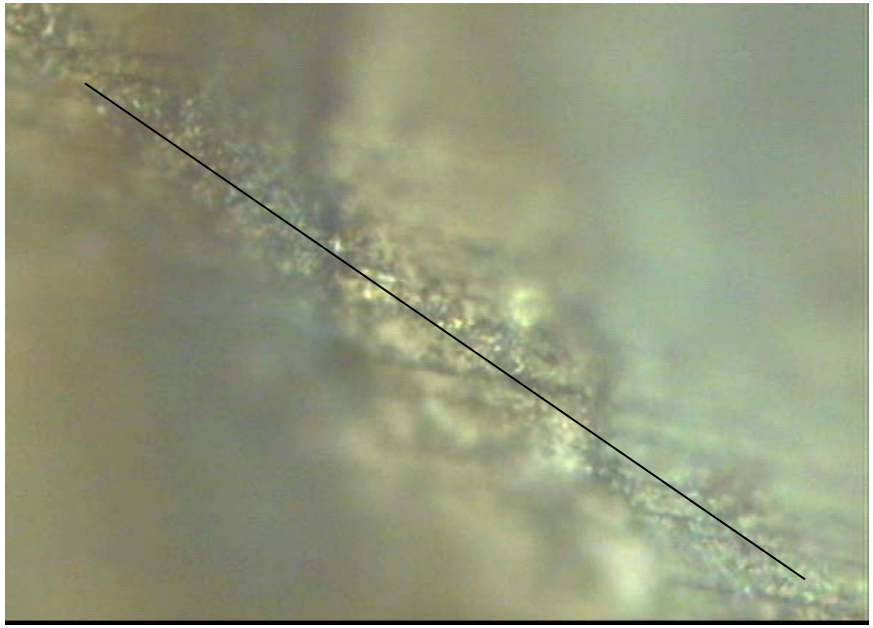
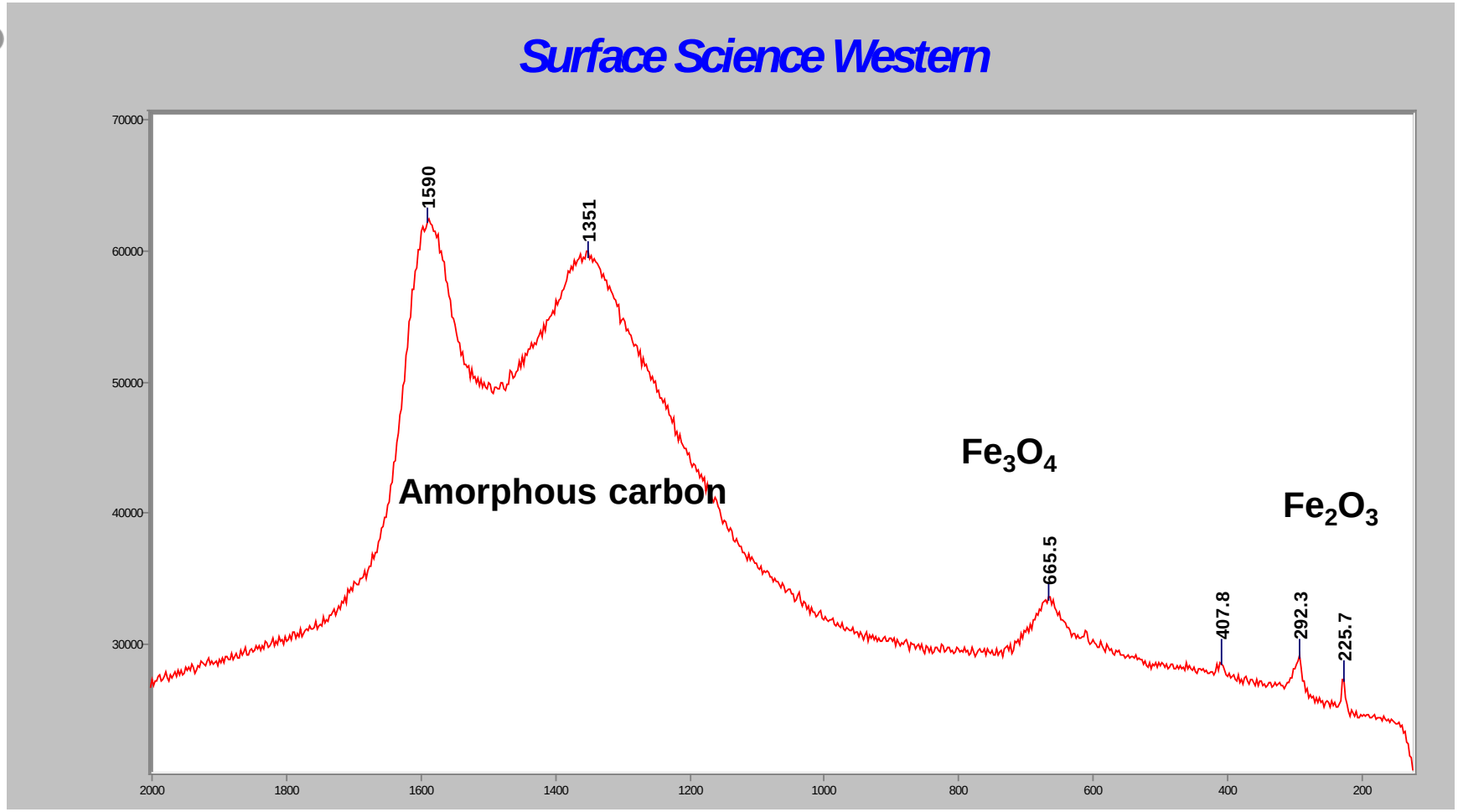
CORROSION PRODUCTS ON STEEL SAMPLES

PROBLEM: A layer of corrosion product was forming on a steel substrate and the EDX analysis showed a varying composition. The client wanted to know the type and form of the corrosion product.



APPROACH: The sample was analysed in line mode using Raman spectroscopy as Raman is very sensitive to the different forms of iron oxides.

A variety of species were identified using a 1-2 micron spot size



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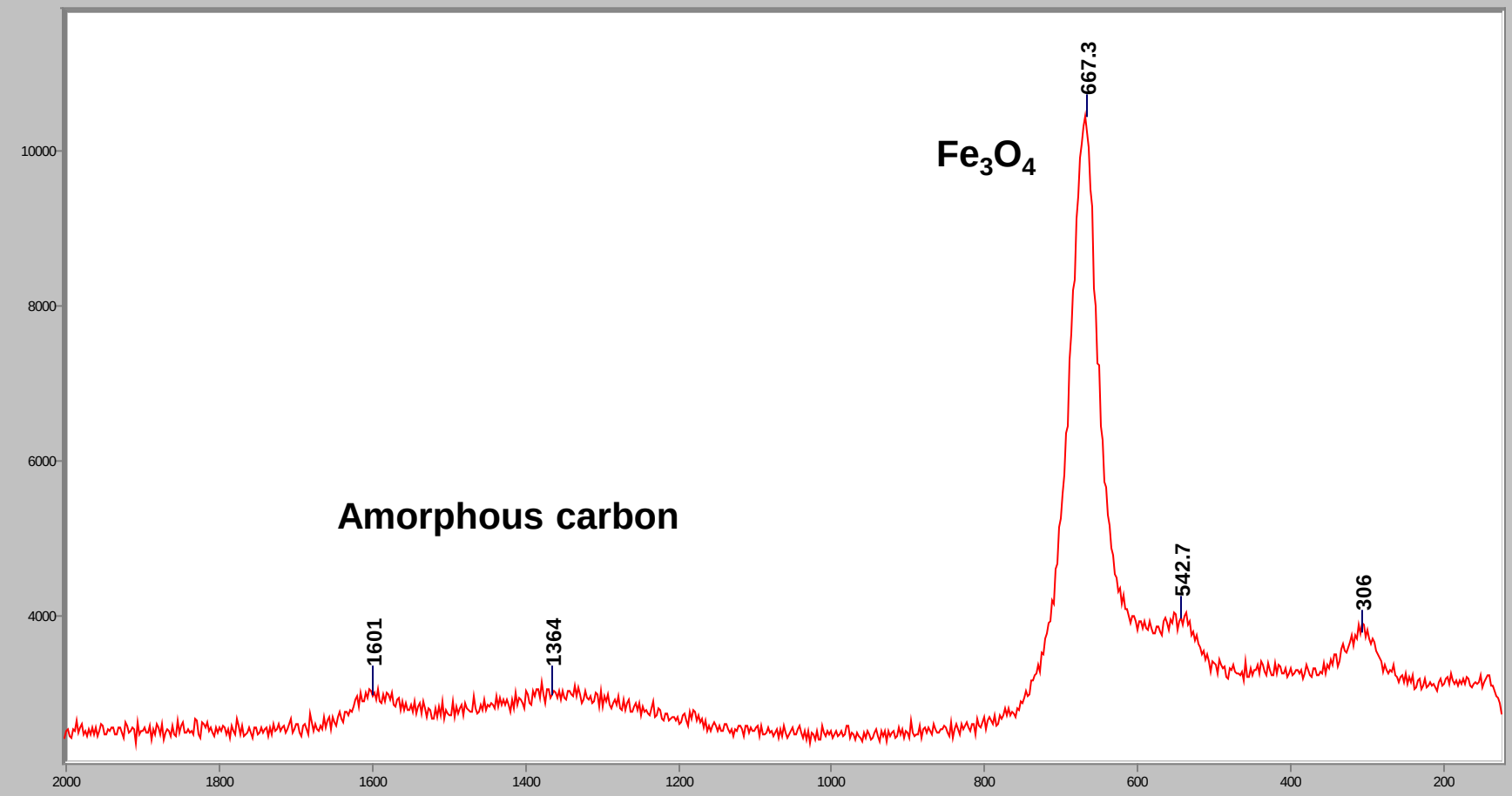

Counts / Raman Shift (cm-1)

Overlay Z-Zoom CURSOR

File # 1 : LINE6#8 @8 Microns

5/14/2008 8:41 AM Res=None

13008 KIN R46 C64, LINE SCAN

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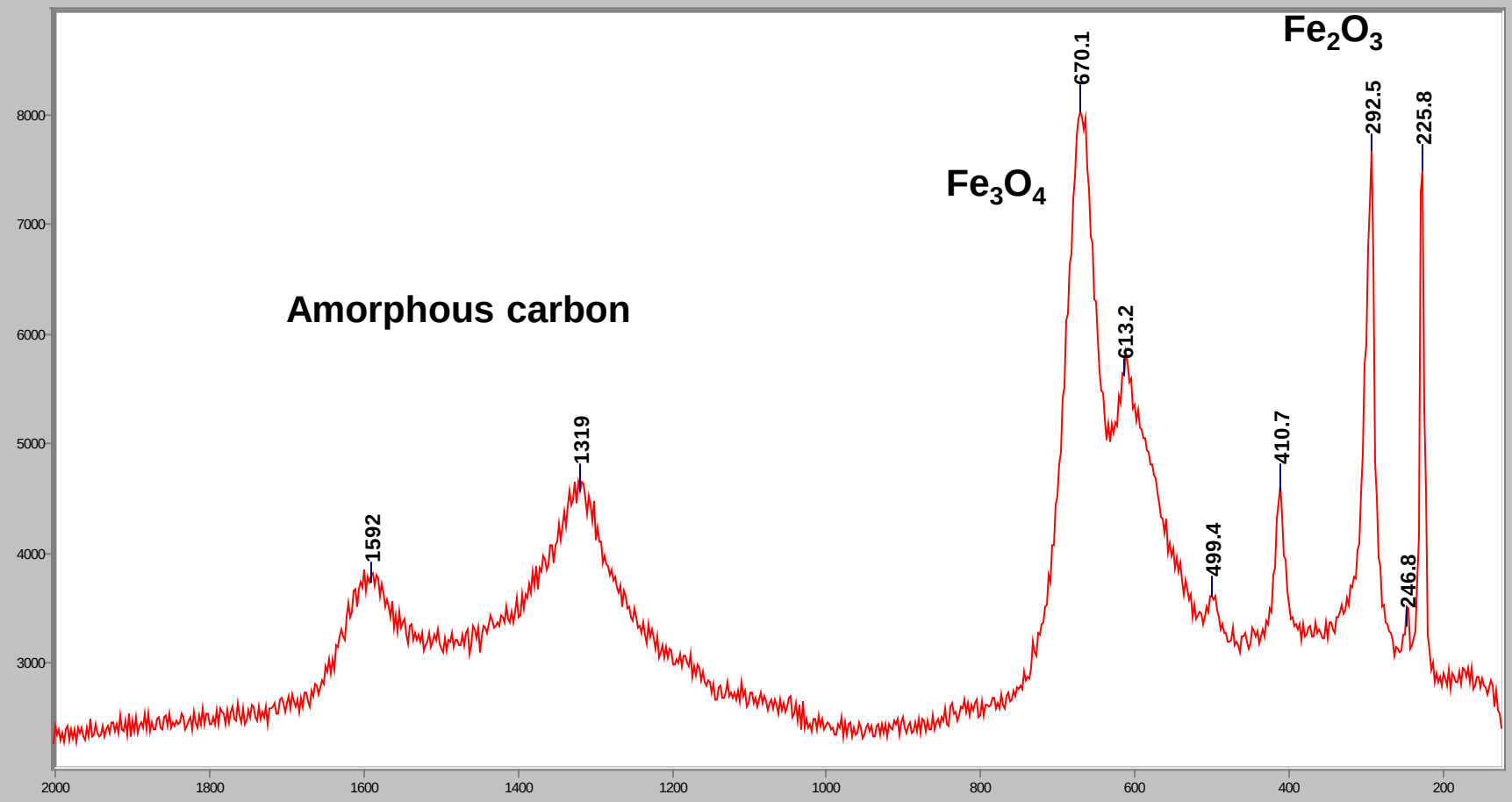

Counts / Raman Shift (cm-1)

Overlay Z-Zoom CURSOR

File # 1 : LINE6#15 @15 Microns

5/14/2008 8:41 AM Res=None

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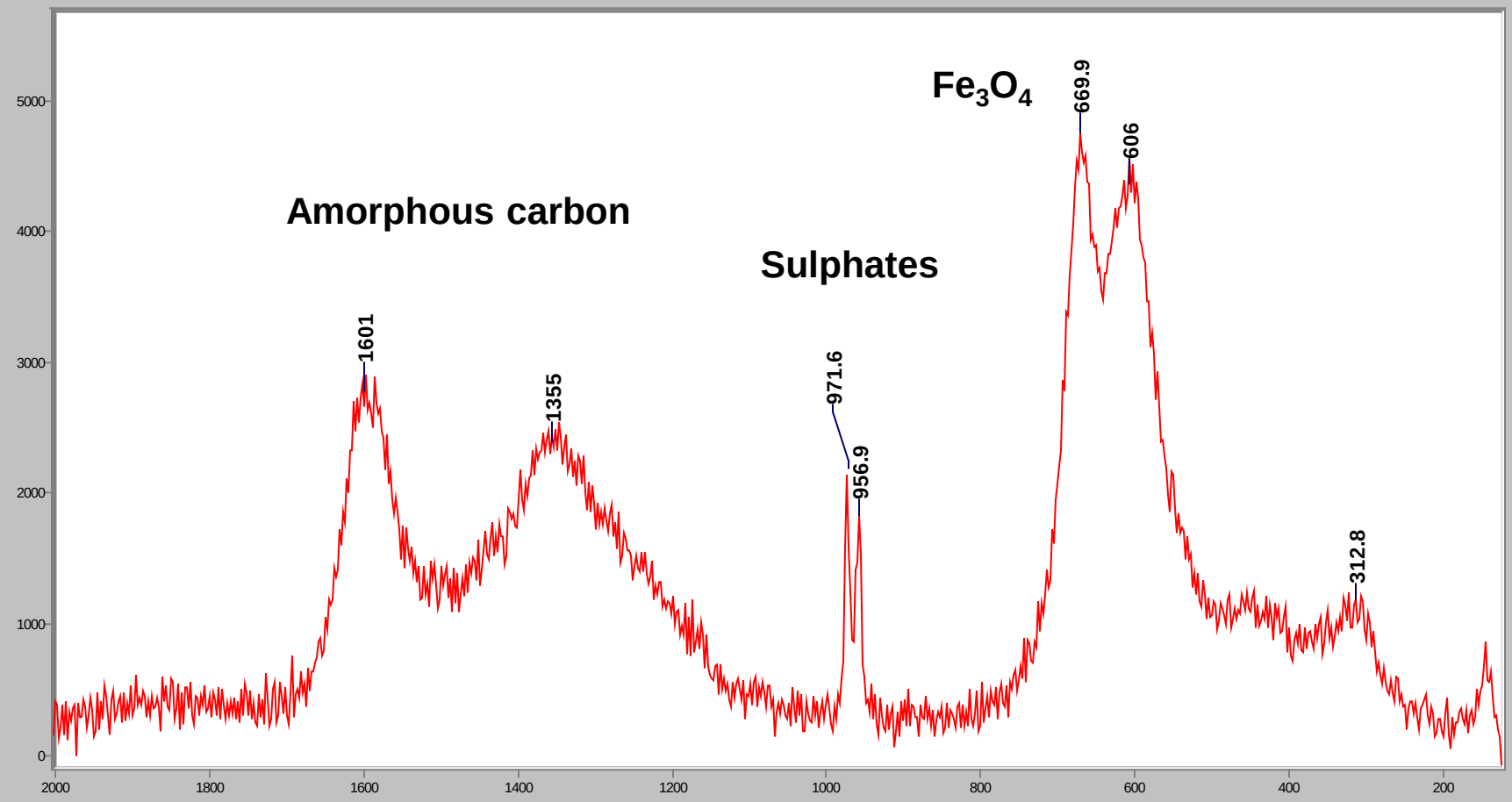

Counts / Raman Shift (cm-1)

Overlay Z-Zoom CURSOR

File # 1 : BASELINE

5/14/2008 8:41 AM Res=None

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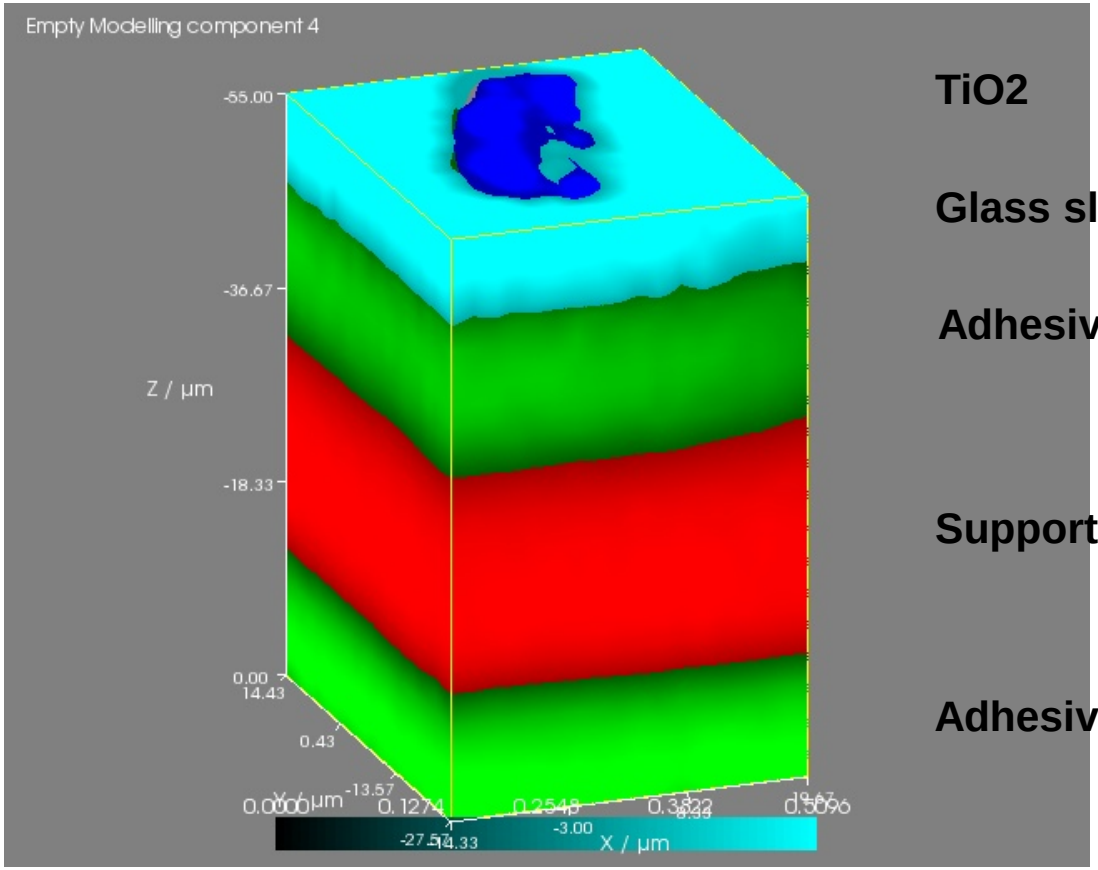
Volume analysis by Raman



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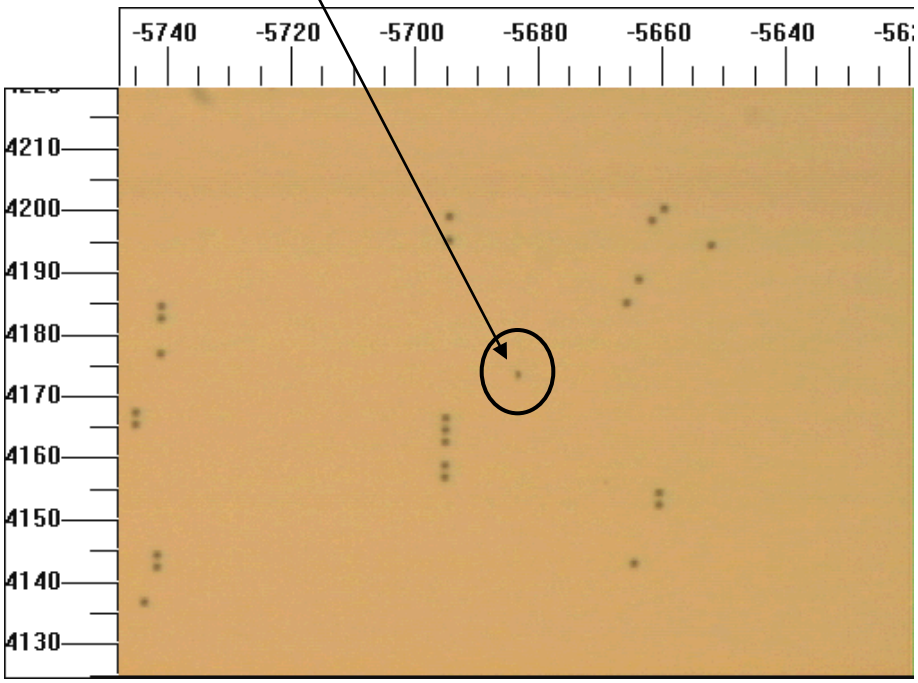
ANALYSIS OF MICRON-SIZED DEFECTS ON PHOTOMASKS

Photomasks are highly detailed quartz plates used to generate patterns on silicon chips. Very small defects on the photomask can cause very expensive problems on the chips. Because of the size of the defects (~1 micron) they are very difficult to characterize.

Using a Raman spectrometer equipped with an ultra long working length objective and a very sensitive xyz motorized stage we have been able to locate and analyze these defects, working directly through the protective pellicle, doing no damage to the photomask and without further contamination.



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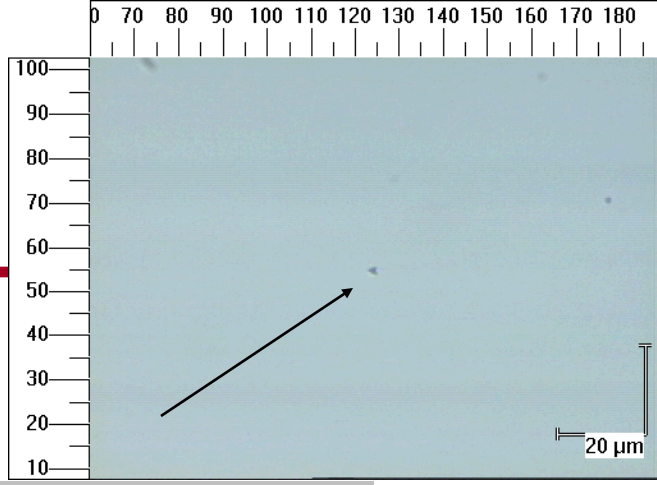
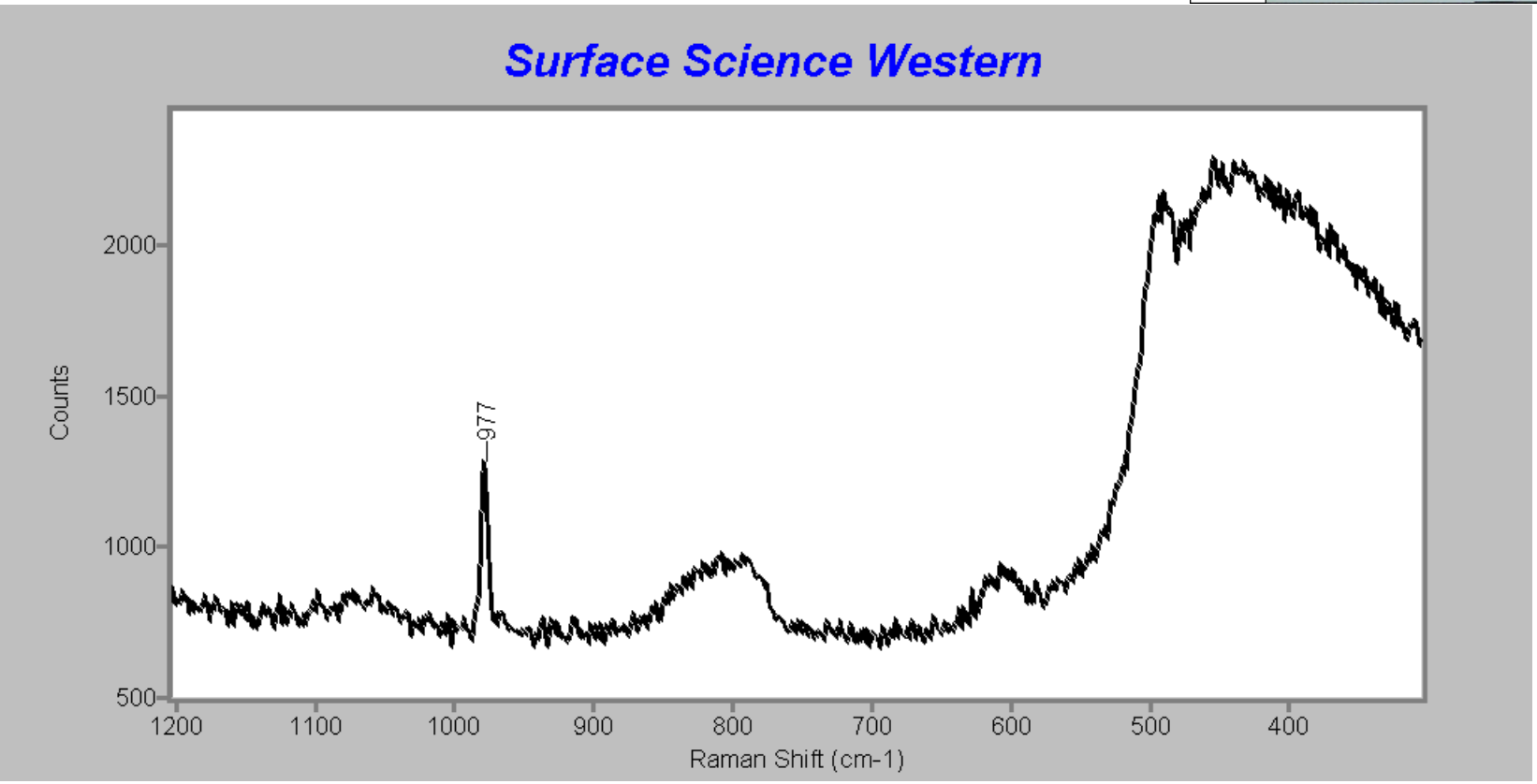
Particle approximately a micron in size





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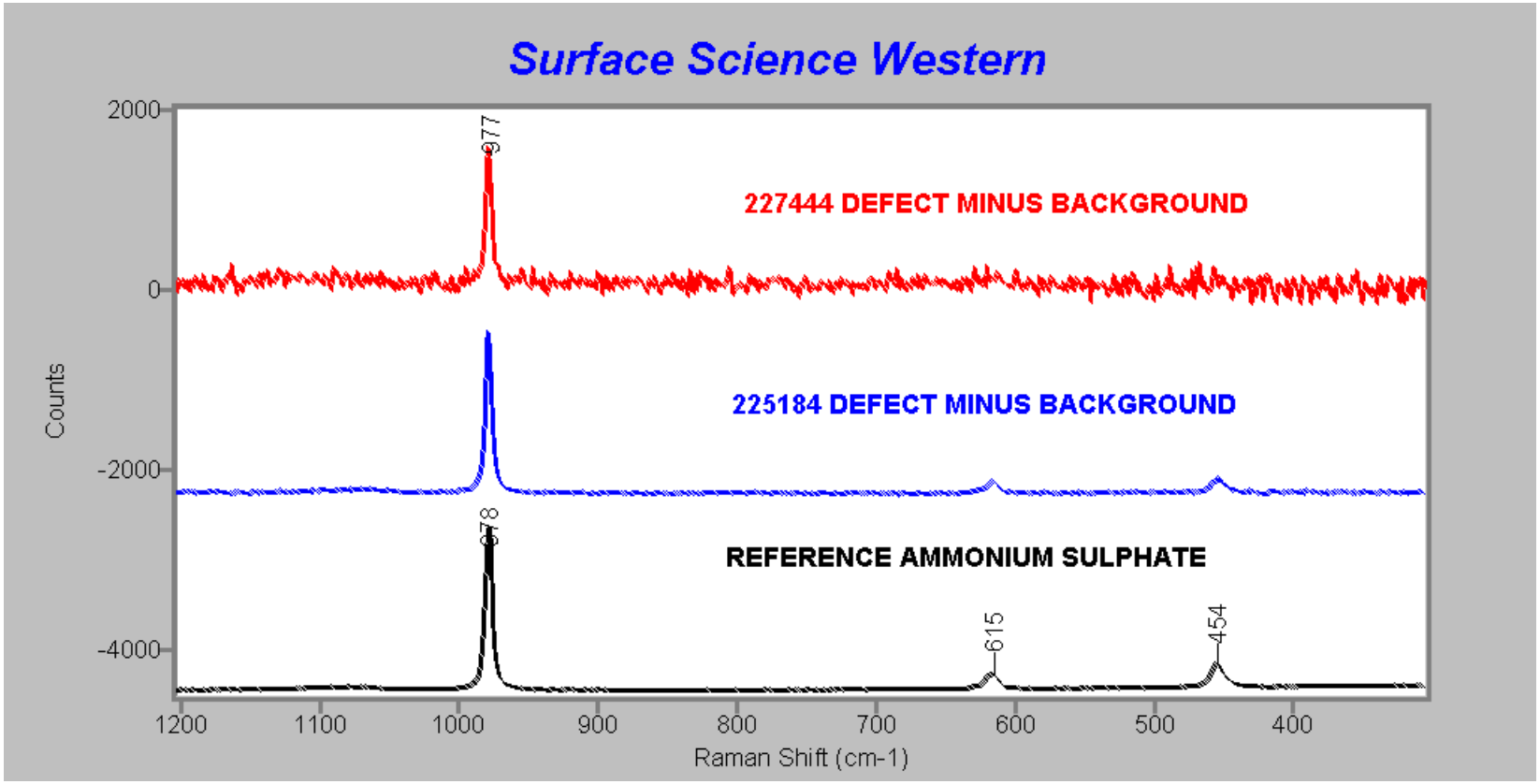

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Summary

- Both FTIR and Raman are vibrational spectroscopies that allow one to examine the bonding in materials. The spectra are characteristic of the material and allow identification.
- FTIR is much more common, has better libraries available and can be quantitative.
- Raman has a much better spatial resolution and can more easily be used to examine metal oxides and crystal structures.