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HazMatID™ Chemical Identifier

Training Course:

Infrared Spectroscopy for Hazardous Materials Identification

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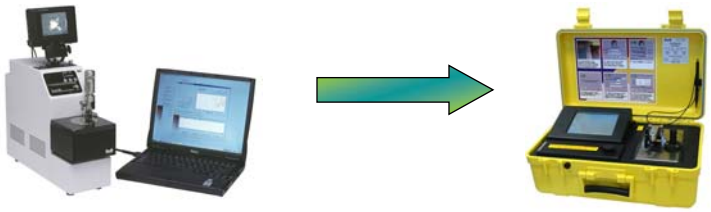
HazMatID Training Course – Outline

1. Basics
   a. Intro
   b. What it can and cannot identify?
   c. How does it identify chemicals?
   d. Wireless operation
   e. Measurement Procedure
   f. Recognizing Good Data
   g. Mixtures
   h. Support
   i. Methods
   j. Libraries
   k. Reports
   l. Maintenance
2. Practical Operation
3. Exam
4. Evaluation

History of HazMatID

- **In 2001, SensIR Technologies introduced the Travel*IR*, the first portable FT-IR spectrometer**
  - **Widely used for the identification of unknown materials including: WMD's, TICS, Common Chemicals, Explosives, Narcotics, *etc.***
- **In 2003, SensIR developed the HazMatID based on feedback from First Responders and the U.S. Military**
- **Hazardous Material Identifier (*HazMatID*) is an entirely new concept for in field-based Fourier Transform Infrared (FT-IR) spectroscopy**



"What is Infrared Spectroscopy" ?

- **Spectroscopy is**
  - ***The study of how electromagnetic radiation interacts with the atoms and molecules that make up matter***
- **A Spectrum is**
  - ***A graph of how much infrared light is absorbed by molecules at each frequency***

"Infrared Spectroscopy"

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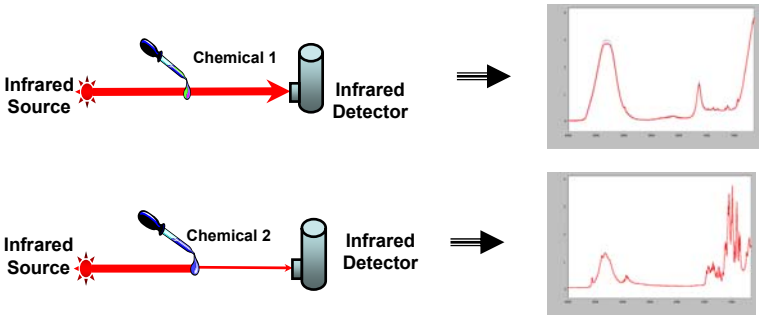
- Chemicals absorb infrared light.
- The pattern of absorption is unique to a chemical.
  - Pattern is called a Spectrum.
- HazMatID will match the spectrum of the sample to a library.



Infrared Radiation

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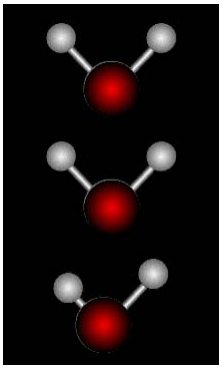
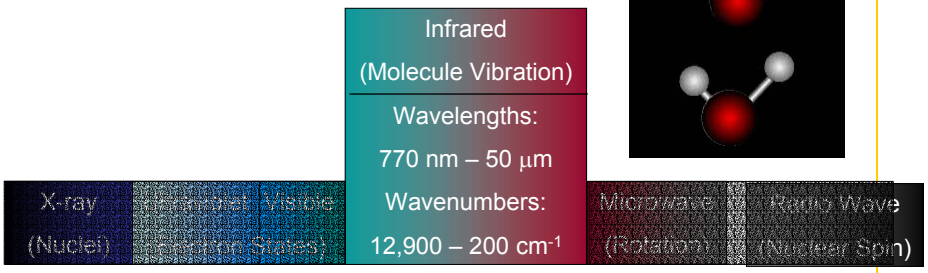
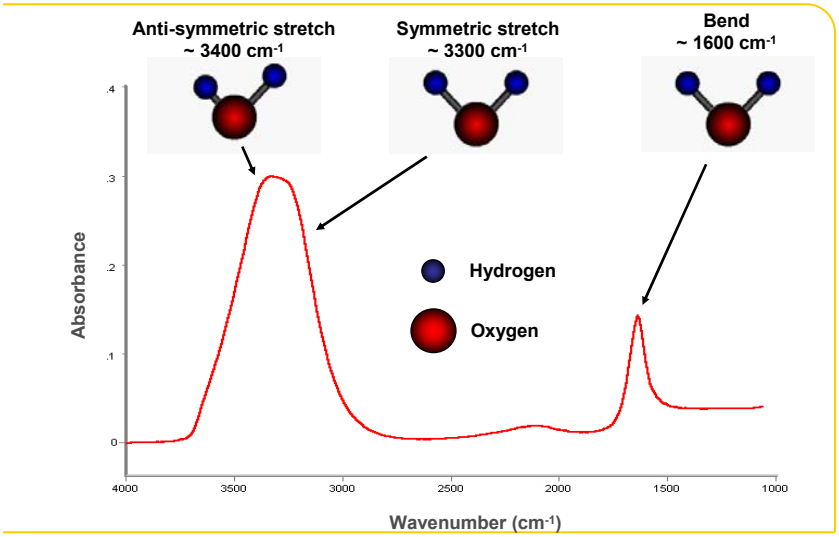
- **Wavelengths of light in the infrared (heat) region have energies that are on the same order of magnitude as *vibrating bonds* in molecules**

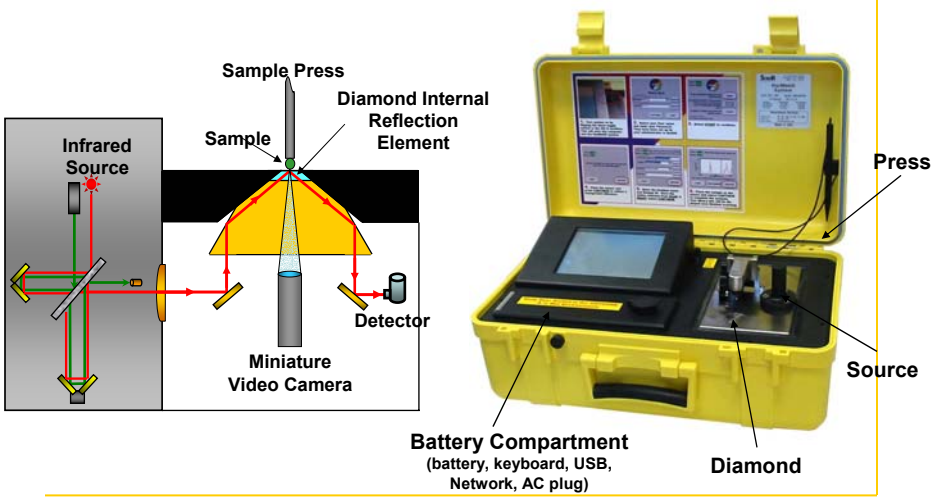




Infrared Spectrum of Water (H_2O)

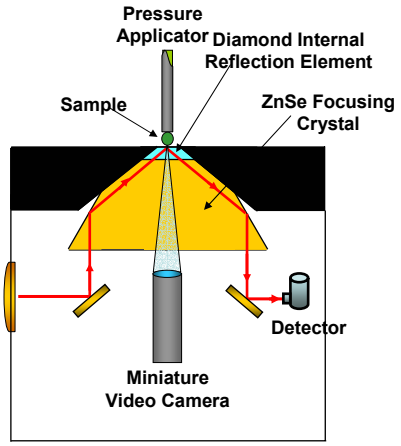


HazMatID Main Components



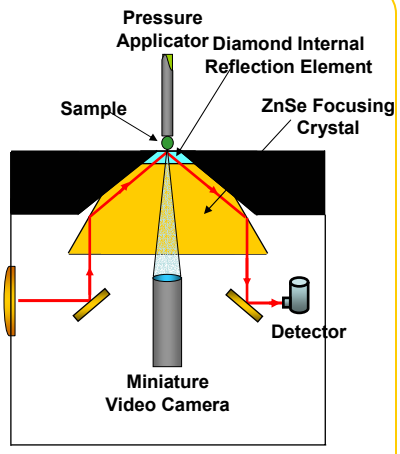
Diamond ATR Advantages

- Easy sampling
  - Solids, liquids, paste
- Consistent sampling
  - Path length controlled by ATR crystal
- Easy clean up
- Diamond
  - Chemical resistant
  - Scratch proof
  - Strong (10,000 psi applied pressure)



Diamond ATR Features

- IR penetrates sample very small amount
  - 0.0015mm for most chemicals
  - Sample thickness doesn't matter
- Liquids coat the surface
- Solids must be pressed against the surface



What can the HazMatID Identify ?

- **Solids, liquids, and pastes**
- **Must have a COVALENT CHEMICAL BOND**
  - **Organic compounds**
    - **Petroleum products, Pesticides, Fertilizers, Plastics, Plant materials**
  - **Many inorganic compounds**
    - **Water**
    - **Mineral acids (sulfuric, nitric, *etc*.)**
    - **Inorganic oxides (rust, talc, *etc*.)**
    - **Nitrates, Chlorates and Phosphates.**

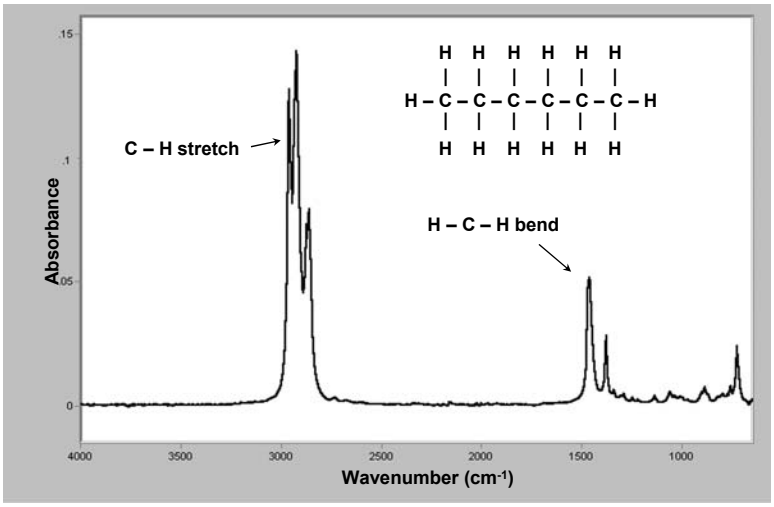
What can the HazMatID NOT Identify ?

- **Elemental substances**
  - **Metals (iron, aluminum, *etc*.)**
  - **Non-metals (sulfur, phosphorus, *etc*.)**
- **Ionic salts (sodium chloride, calcium chloride)**
- **Dilute aqueous (water-based) solutions, or individual components of any mixture**
  - **Less than 10% concentration**
- **Biological Agents**
  - **Infrared Spectroscopy as a field based portable analytical technique (HazMatID) can NOT definitively identify biological agents.**

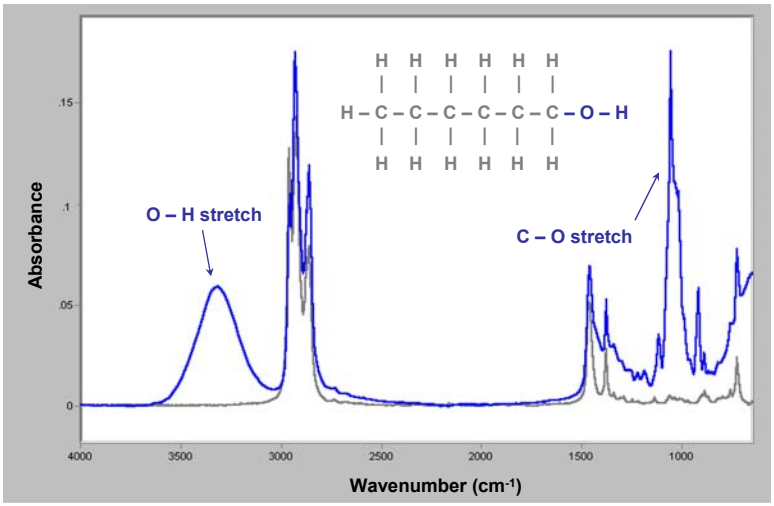
How does it identify chemicals?

- **Recall that an infrared spectrum has peaks where light energy is absorbed by molecular bonds**
- **Bonds between particular atoms (functional groups) occur at characteristic wavenumbers**
- **Let's look at the effects some functional groups have on infrared spectra ...**

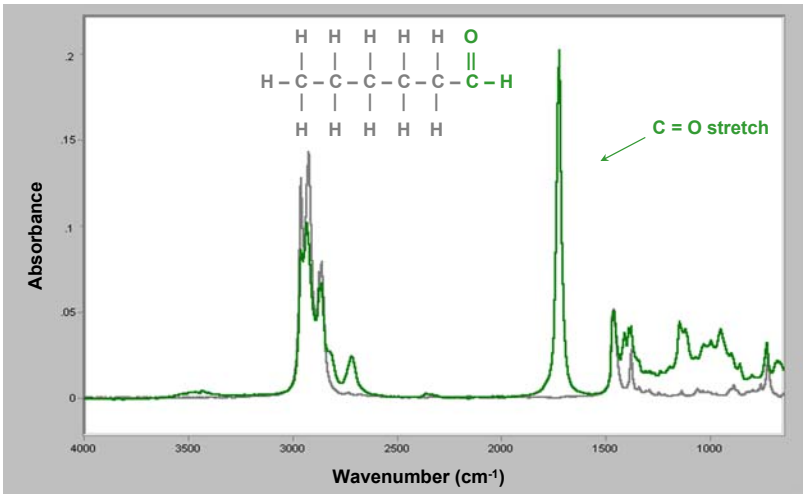
Hexane



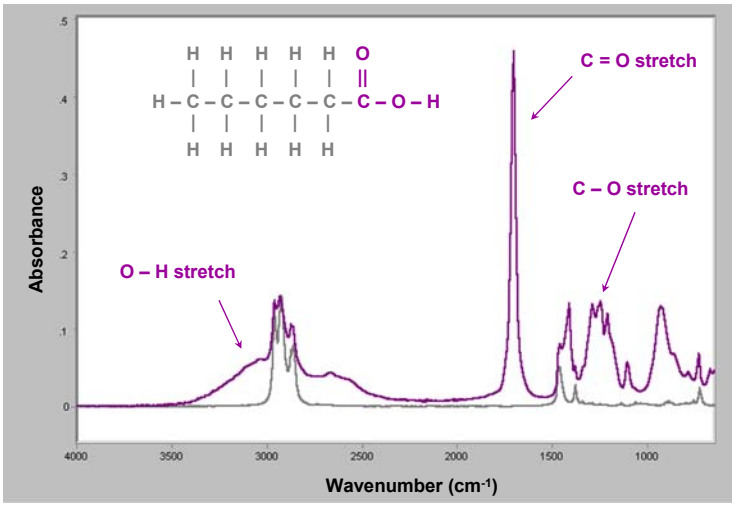
Hexanol



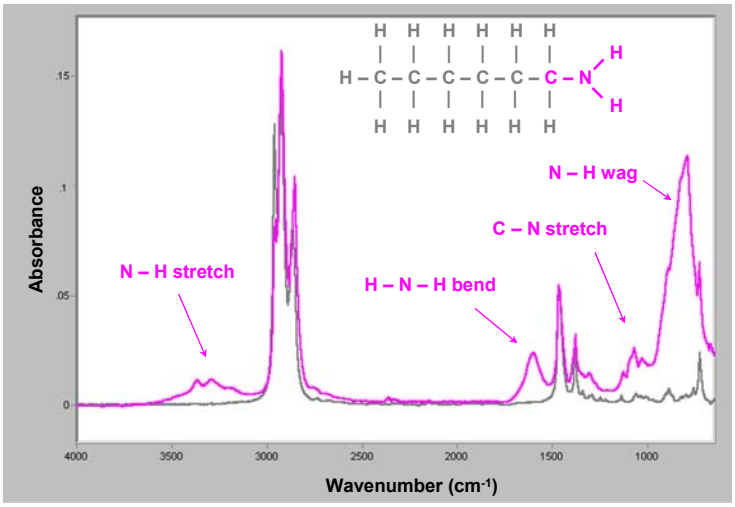
Hexanal



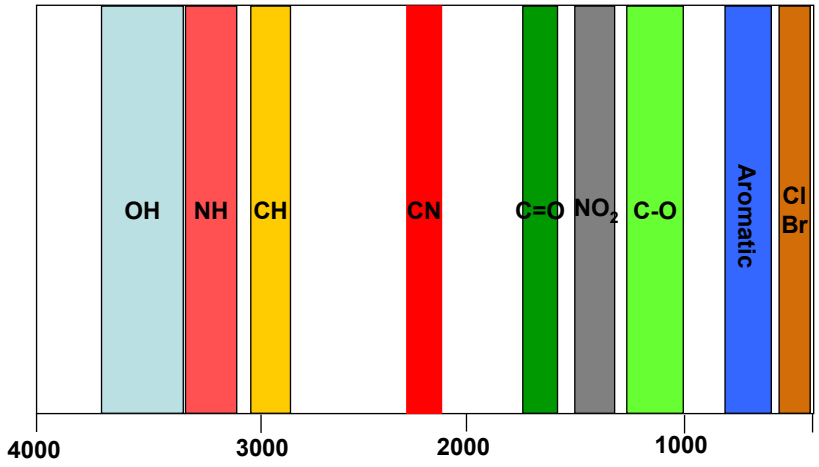
Hexanoic acid



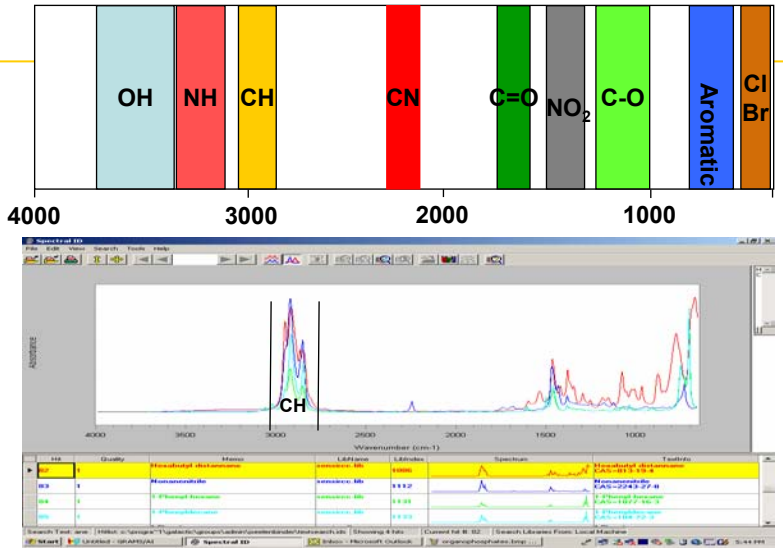
Hexyl amine



Absorption Landmarks

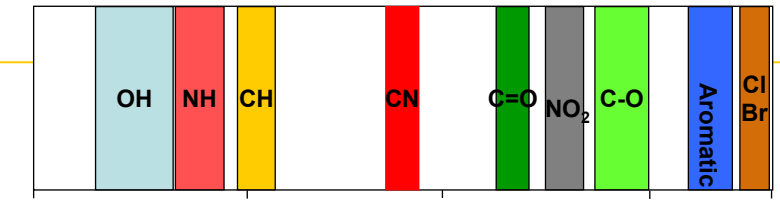


Hydrocarbon



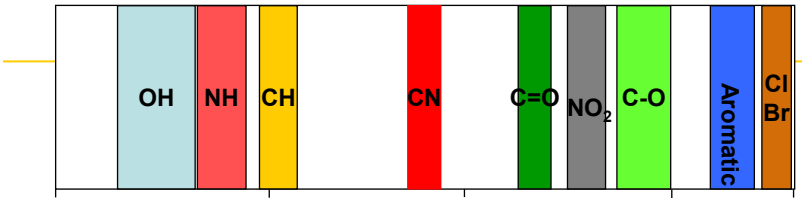
Alkane (CH, hydrocarbon)

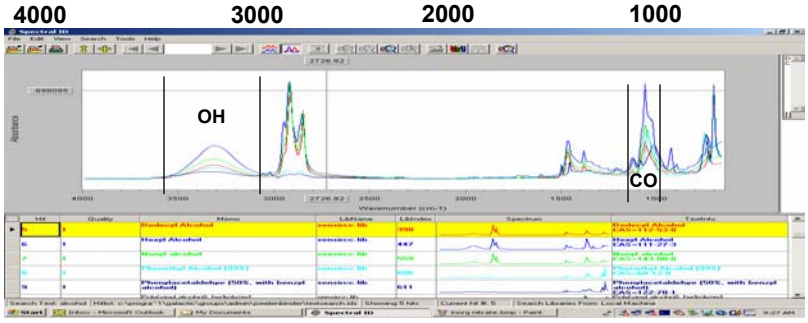
Aromatic (xylene)



Aromatic (xylene)

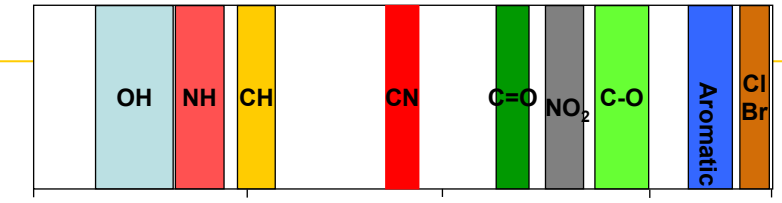
Alcohol

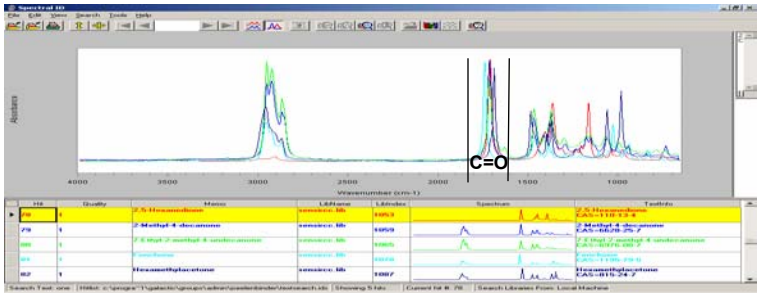




Alcohol (C-O, OH)

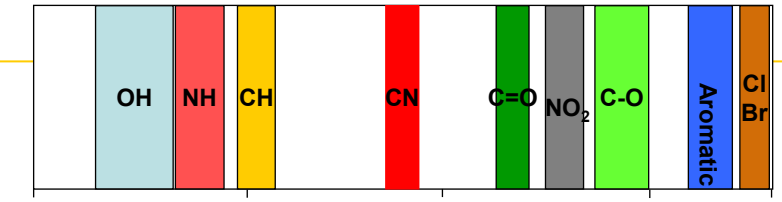
Carbonyl

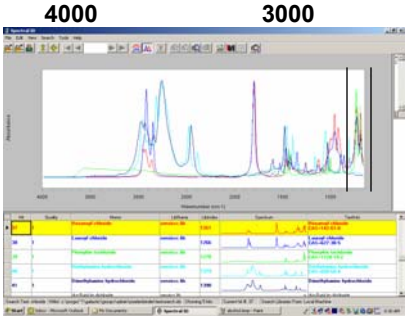




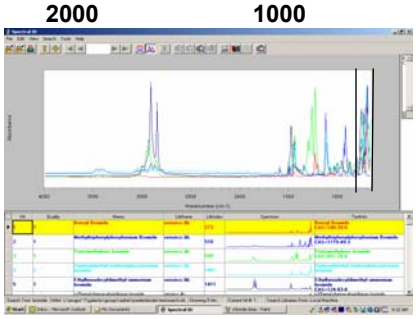
Ketone (C=O)

Halogens



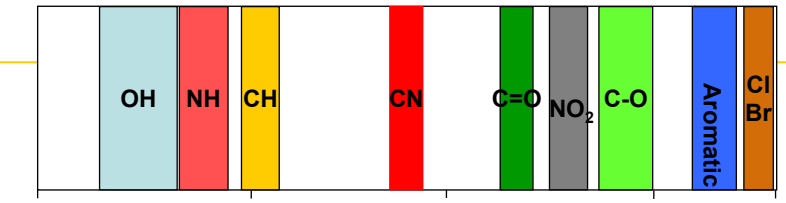


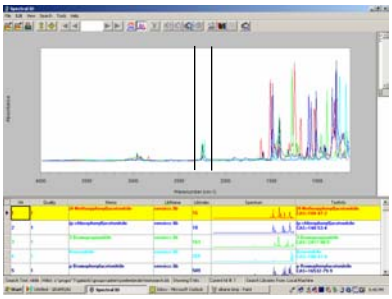
Chloride (C-Cl)



Bromide (C-Br)

Nitrile, Isocyanate



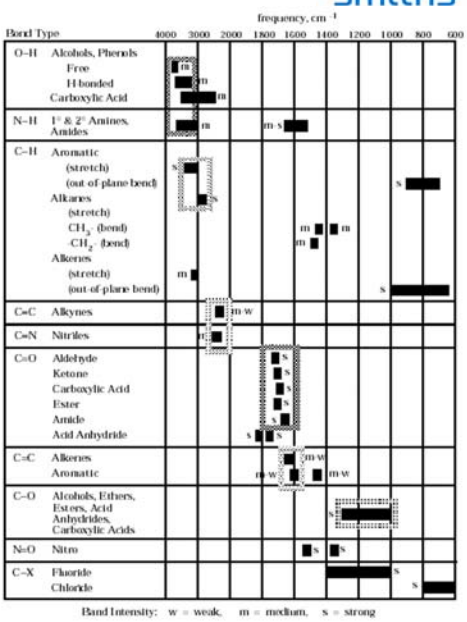


Nitrile (CN)

Isocyanate

Correlation Chart

- **Chemical bonds have absorption bands at very characteristic wavenumbers (cm^{-1})**
- **With practice, one can classify a chemical just by looking at its spectrum**



Molecular "Fingerprinting"

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- **Because chemicals have unique chemical structures, they also have *unique infrared spectra***
- **Just like criminals are identified by searching human fingerprints in databases, chemicals are identified by matching infrared spectra**
- **This matching is done automatically by the HazMat*ID* software**

Molecular "Fingerprinting"

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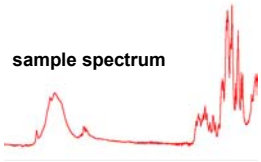

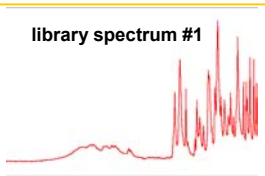

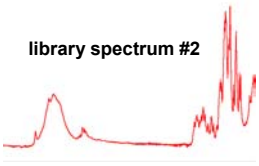

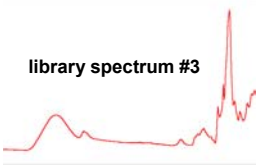

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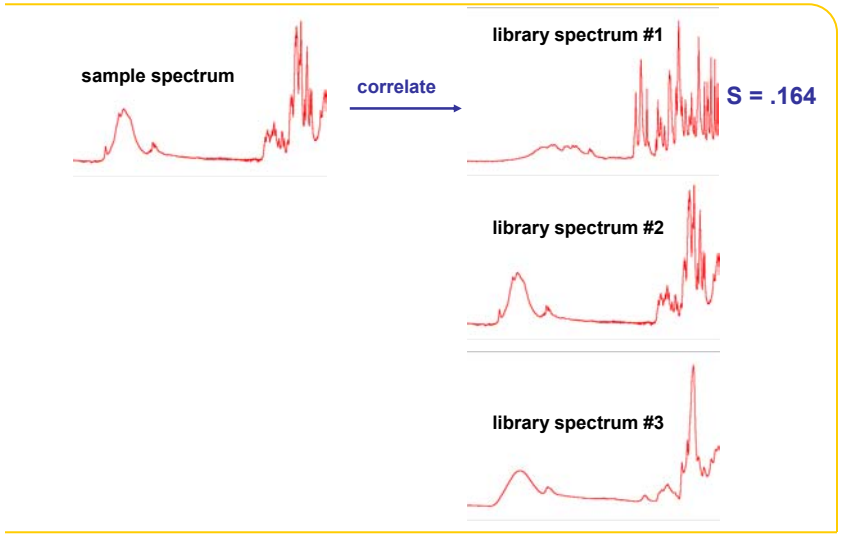
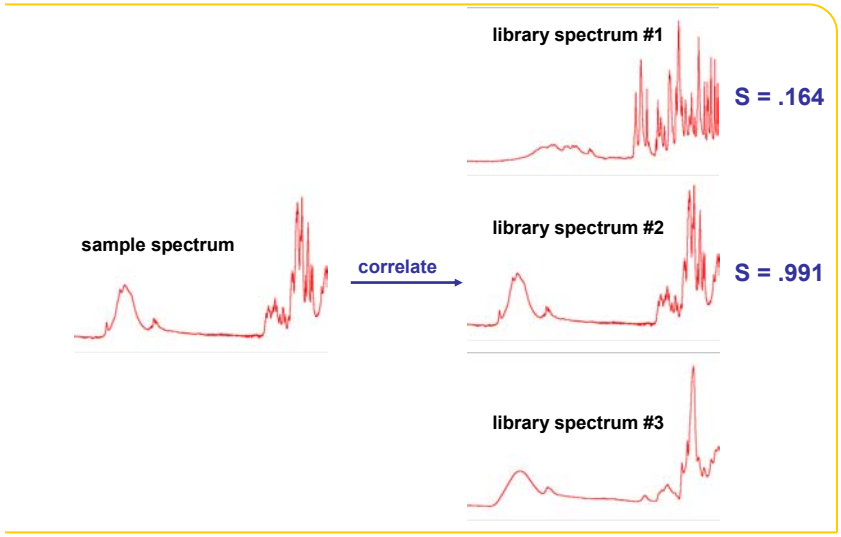
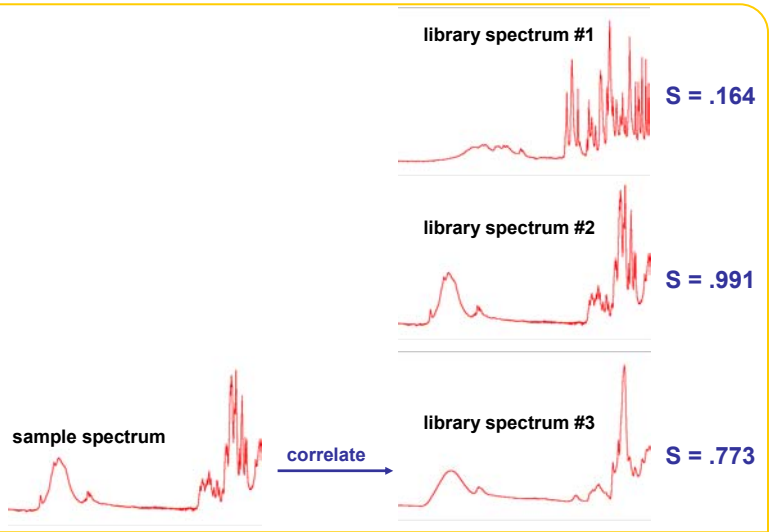


Molecular "Fingerprinting"



Molecular "Fingerprinting"



Molecular "Fingerprinting"

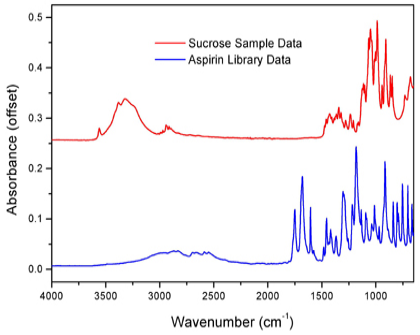
- **Once the "unknown" sample spectrum is compared to all available library spectra, the results are ranked:**

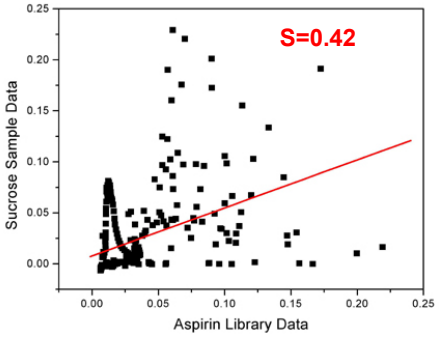
Library Spectrum #	Correlation Value (Similarity)
2	.991
3	.773
1	.164

The library spectrum with the *highest* correlation value is the *most likely* identity of the unknown

What is "Correlation" ?

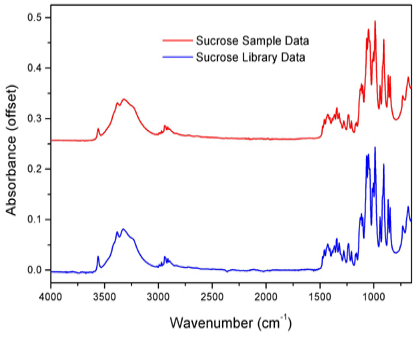
Different Substances = Poor Correlation = Low S Value

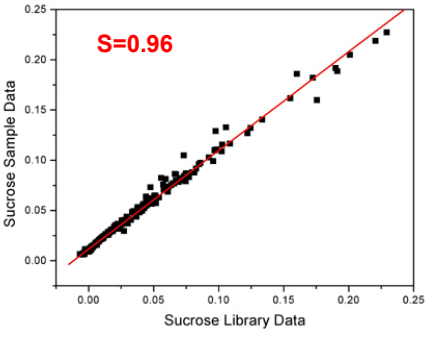




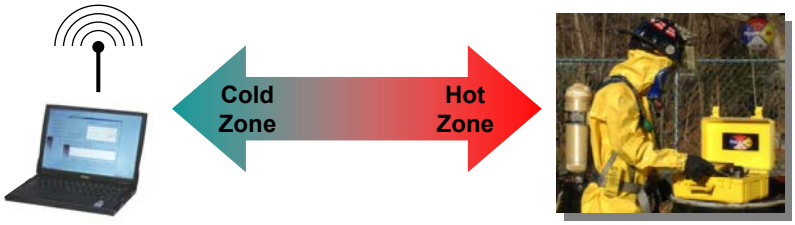
What is "Correlation" ?

Similar Substances = Good Correlation = High S Value





HazMatID Wireless Communication



- Transfer files to Laptop or Desktop over wireless network, or Control HazMatID software remotely with PC Anywhere™
- 128 bit WEP encryption security capable
- Compliant with 802.11b standards
- Operating Range depends on connection speed and environmental conditions
  - Outdoors up to 150 feet

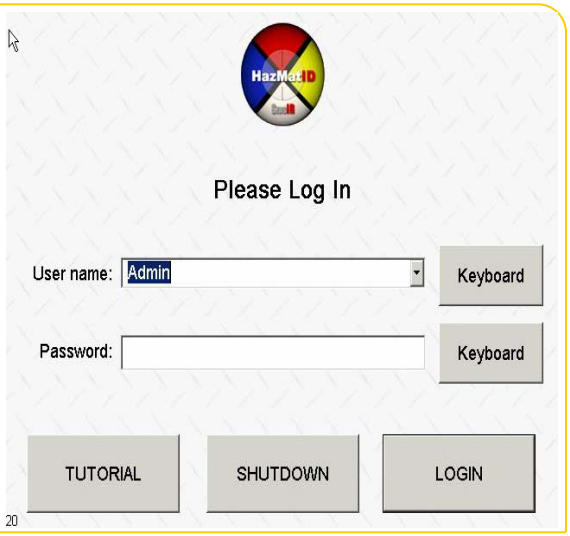
Smiths/SensIR: Libraries

Included	
Common Laboratory Chemicals	3302 spectra
Common Household White Powders	41 spectra
Regulated Drug Precursors (Meth Lab)	43 spectra
Toxic Industrial Chemicals (NIOSH Guide)	383 spectra
Forensic Drugs (IL State Police)	454 spectra
Explosives (CO State Forensic Lab)	31 spectra
Chemical Warfare Agents (4th WMD CST)	7 spectra
	4261 spectra

Additional Available Libraries	
Sigma-Aldrich™ ATR Library	18,513 spectra
Pesticide Active Ingredients	273 spectra
IChem™ ATR Library	12,706 spectra
IChem/Aldrich Combined Library	26,221 spectra

Powering Up the HazMatID System

- **Insert a battery or connect the system to AC power using the AC adapter.**
- **After the system boots up, the login screen will appear.**
- **The default login screen name is: Admin with no password**
- **Approx. 1 minute after this screen appears the wireless is available**



Measurement Procedure

- **Clean diamond**
  - **Last rinse with methanol, rubbing alcohol or acetone**
  - **Make sure diamond is dry before continuing**
- **Measure Background**
  - **Should be as close to sample measurement as possible**
- **Apply Sample**
  - **Observe flat baseline**
  - **Add sample**
  - **Pressure if solid, cover if liquid**
- **Record Sample**

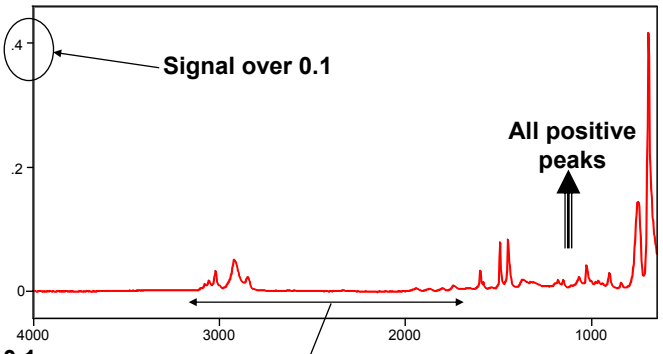
What is a good match?

- 3 criteria for a positive identification
  - Quality (correlation) over 0.95
  - Sample and library match VISUALLY
  - PHYSICAL properties match

What If I Don't Get a Match ?

- Most matching problems fall into 2 categories
  - Spectral Artifacts
    - Baseline problems
    - Easily recognized
    - Minimized by proper procedure
  - Mixtures
    - Primary component match
    - Mathematical subtraction
    - Mixture in the library

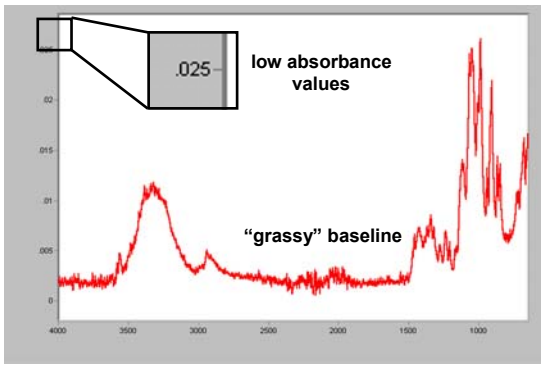
What does a good spectrum look like?



-Signal > 0.1
-Flat, smooth baseline
-All peaks positive

Spectral Artifacts – Poor Contact

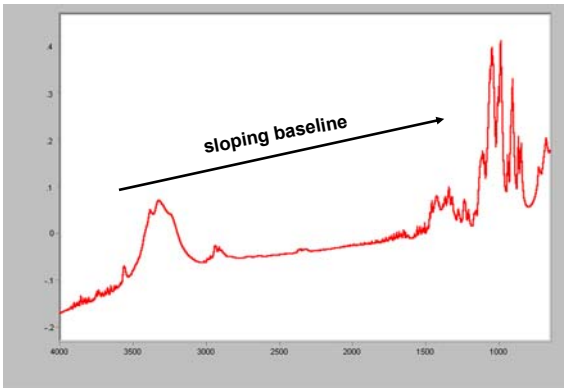
Problem: **Lot of "grass" or "noise" in spectrum, and maximum absorbance value is much less than 0.1**



Solution: **Insufficient amount of sample and/or applied pressure. Make sure sample covers diamond area, and apply more pressure.**

Spectral Artifacts – Bad Baseline

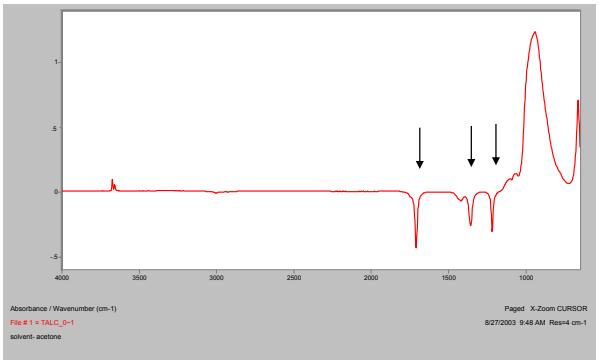
Problem: **Spectrum appears "tilted" at an angle**



Solution: **Background is old. Usually occurs when system has been on for less than 1 hour. Record new background and repeat analysis.**

Spectral Artifacts – Negative Peaks

Problem: **Spectrum has "downward" peaks**



Solution: **Solvent not evaporated from diamond before background measurement. Dry diamond and collect a new background.**

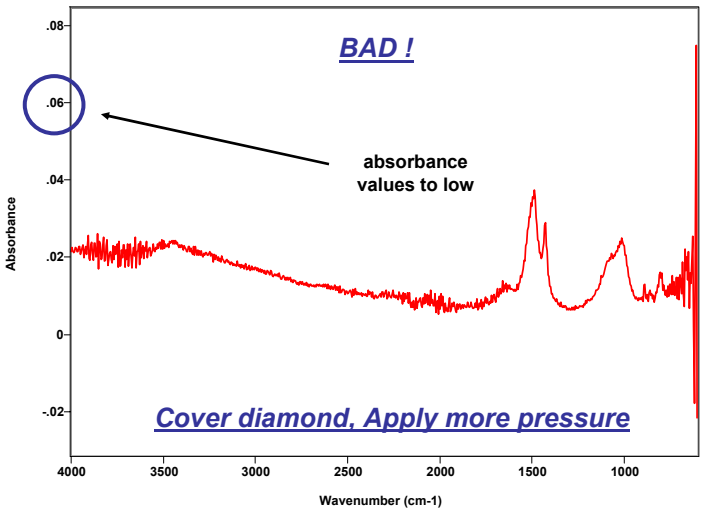
Effect of Artifacts on Library Search

Quality of Sample Sugar Spectrum	Correlation Value to Library Sugar Spectrum
Excellent	S = .997
Poor Contact	S = .989
Bad Baseline	S = .797
Negative Peaks	S = .750

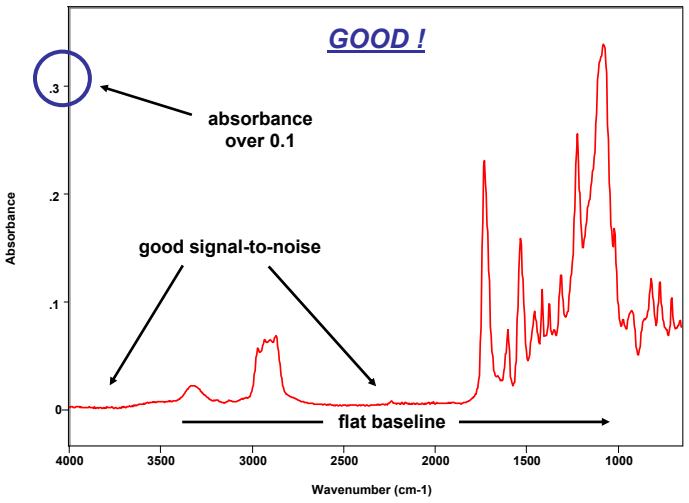
The likelihood of a *positive identification* depends on the *quality* of the data !!!

HazMatID Advanced Topics

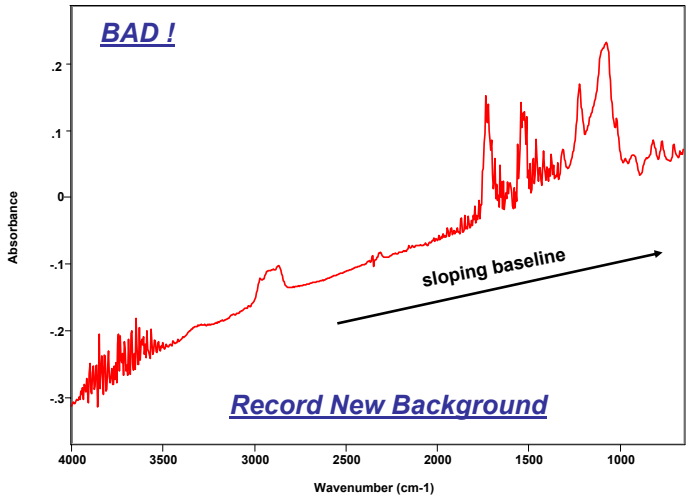
Good or Bad ?



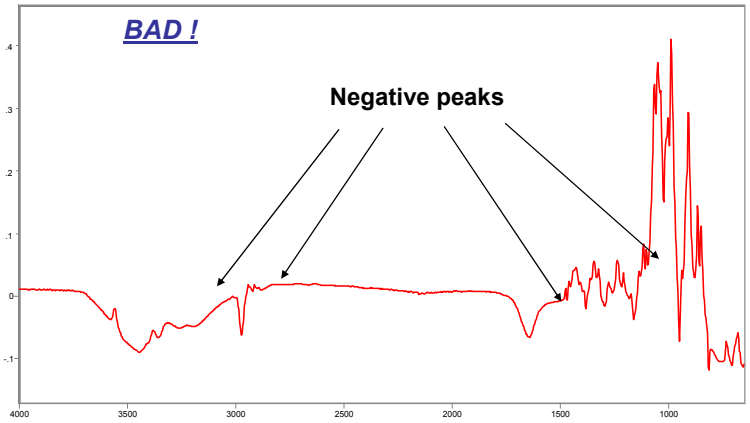
Good or Bad ?



Good or Bad ?



Good or Bad ?



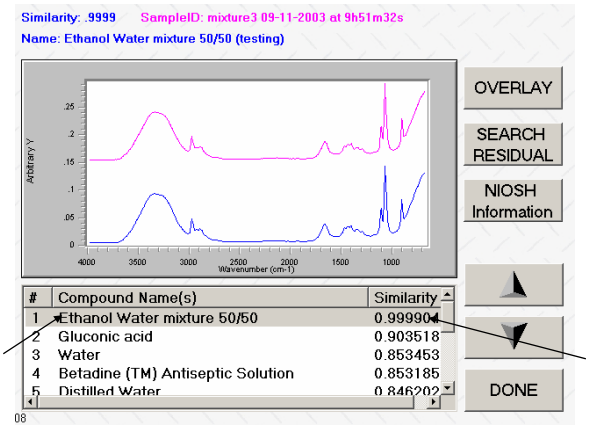
Dry diamond and record new background

HazMatID - Mixtures

- **Unlike GC/MS, Infrared as a technique does NOT separate and identify individual components**
- **Mixtures can be identified with infrared**
  - **The spectrum of a mixture is characteristic of that mixture**
    - If the mixture is in the library, it will match well
  - **Simple mixtures can also be identified by primary component identification and residual mathematical subtraction.**

HazMatID: Mixture Example

Mixture in library

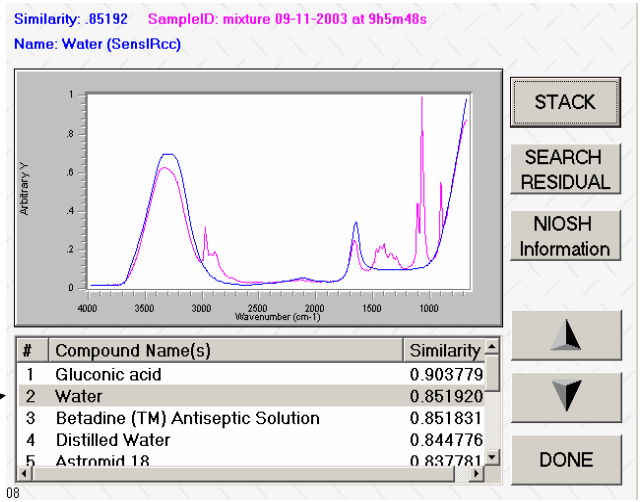


Mixture in library

High similarity

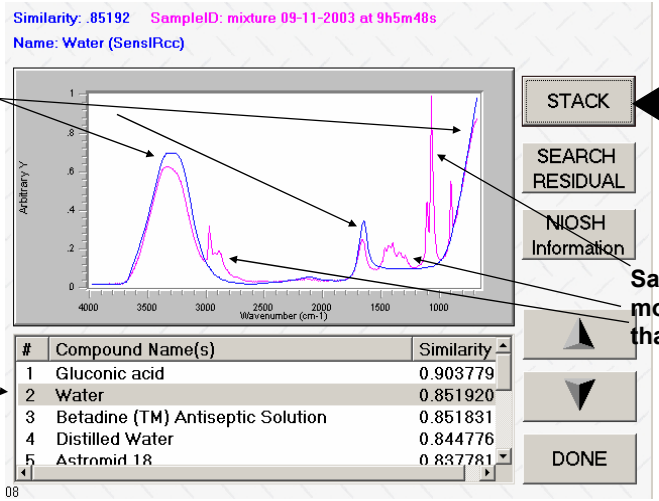
HazMatID - Mixture Example

Mixture not in library



Main component matched but with low similarity

HazMatID: Mixture Example – 50/50 Water, Ethanol

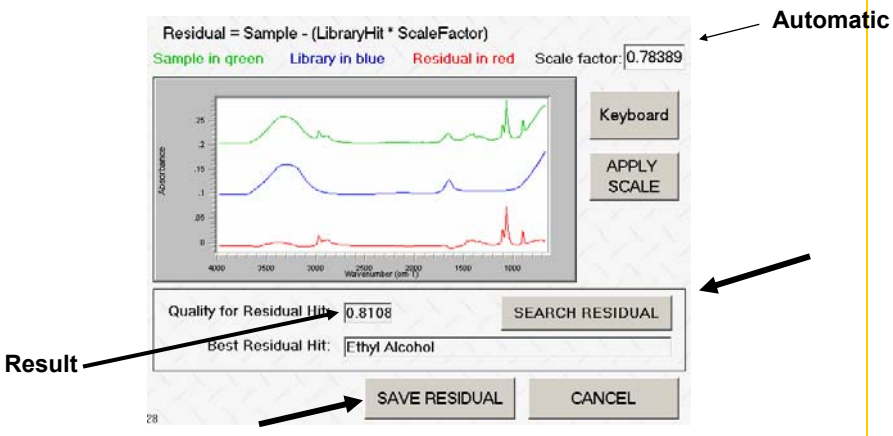


Shape of water seen in sample

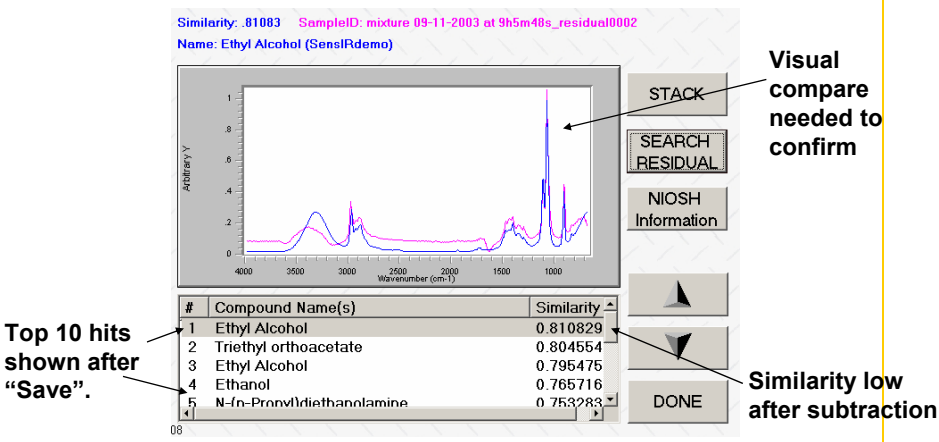
Sample has more peaks than water

Water in top 5 hits

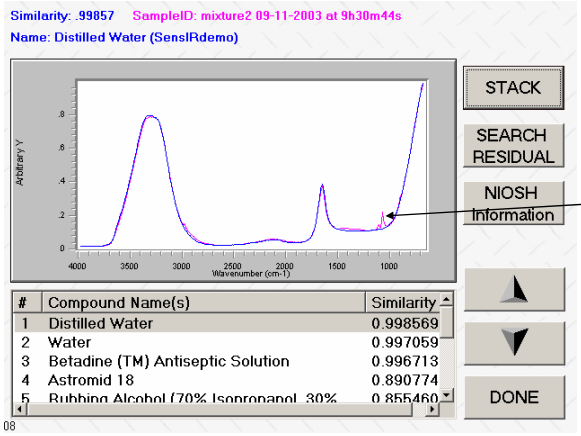
HazMatID: Mixture Example – 50/50 Water, Ethanol



HazMatID: Mixture Example

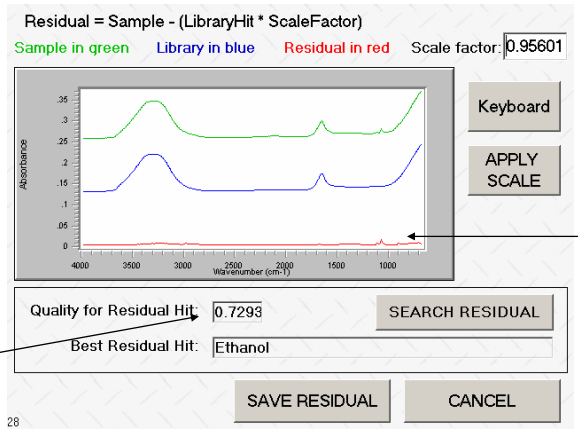


HazMatID: Mixture Example – 90/10 Water, Ethanol



Only small difference noted

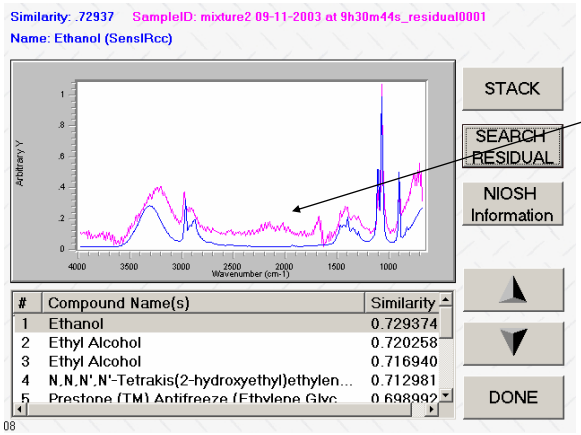
HazMatID: Mixture Example – 90/10 Water, Ethanol



Very little information remaining

Similarity value lower than 50/50 example *0.70 or greater*

HazMatID: Mixture Example – 90/10 Water, Ethanol



Minimum concentration for HazMatID: 10%

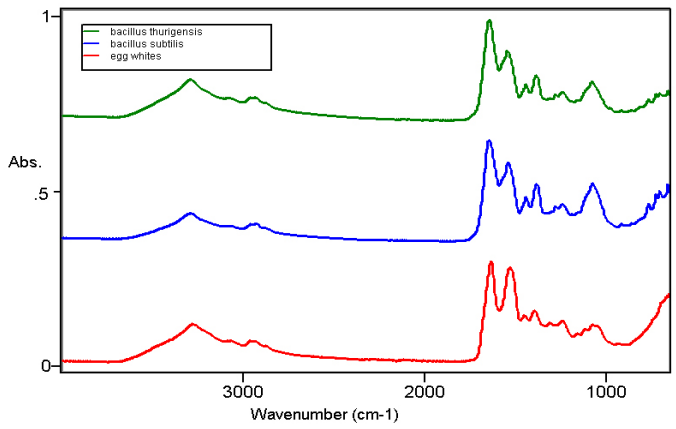
Biological Agents

- Infrared Spectroscopy as a field based portable analytical technique (HazMatID) can **NOT** definitively identify biological agents.
- Why not?

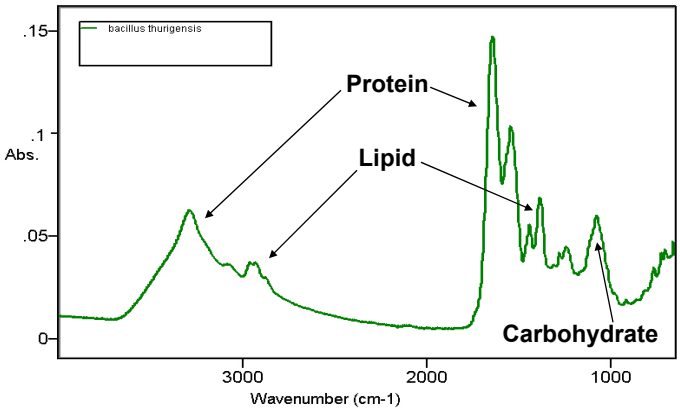
Biological Agents

- Chemistry of bacteria and microorganisms
  - Three main components
    - Protein
    - Lipids
    - Carbohydrate
  - The majority of chemicals (> 80%) in microorganisms are protein.
  - Spectra of proteins are too similar to distinguish using library matching
    - Spectra more dependant on protein preparation than identity
    - Moisture content, media for growth, etc.

Bacterium Comparison



Bacteria Components



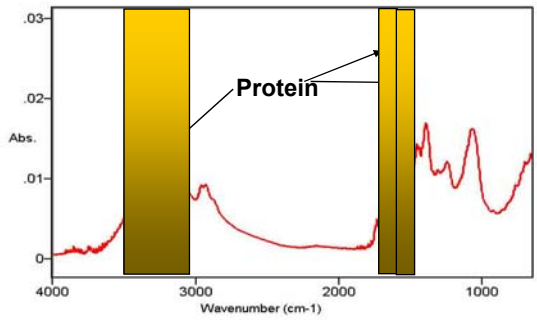
Biological Agents

- **IR spectroscopy can NOT currently positively identify biological agents**
  - **Several Universities researching possibilities**
- **We can detect proteins**
  - **80% of biological agents consist of proteins**
  - **Still limited by the 10% concentration limit**
- **HazMatID has a "Bio Check" with looks for the presence of proteins**
  - **3300 cm^{-1}**
  - **1640 cm^{-1}**
  - **1540 cm^{-1}**

Biological Agents

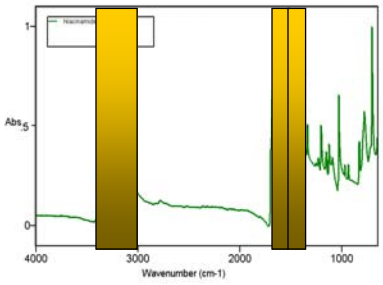
If peaks are found in all three of the bio check regions, a "protein warning" is displayed

Bio Check Regions

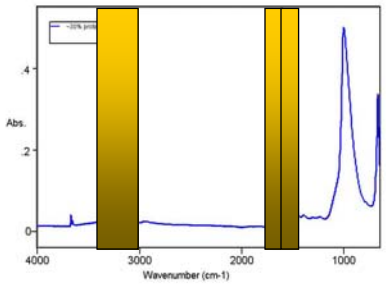


Biological Agents

- **Why do I get false positives?**
  - **False positives are erring on the side of caution**
  - **"Bio Check" is set sensitive to find proteins in a mixture**



Niacinamide – vitamin supplement



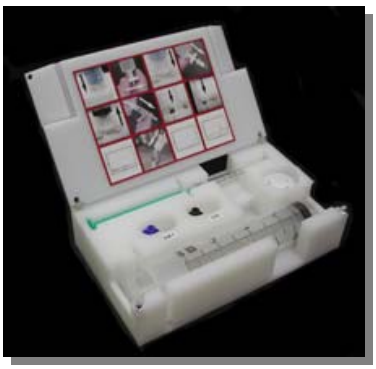
~ 30% Protein in Talc

Biological Agents

- **HazMatID is only an INITIAL screening tool for biological agents.**
- **False positive are possible with the "Bio Check".**
- **To confirm a protein, look for 3 peaks**
  - **3300 cm^{-1}**
  - **1640 cm^{-1}**
  - **1540 cm^{-1}**
- **Remember the 10% concentration limit**

ExtractIR

- **Physically separate mixtures using Solid Phase Extraction (SPE)**
- **Separate non-volatile organic compounds from water in about 10 minutes**
- **Designed for Hot Zone use**
- **Increase detection limits by about 3 orders of magnitude (from 10% to 0.01%)**



24/7 ReachBack

- **Chemists, Spectroscopists, Engineers, and technicians are on call 24 hours a day, 7 days a week for urgent assistance.**
- **If no close match is possible, or other system related problems are incurred, contact Smiths Detection/SensIR ReachBack number:**
  - ***1-866-442-0628 or 1-866-777-8880***
  - **Provide the Operator with the following information**
    - **Name**
    - **Location of Incident**
    - **Environmental conditions (weather, temperature etc.)**
    - **Urgency of Matter**
    - **Sample description – be specific**
    - **Problems (Spectral interpretation assistance, software or equipment, etc.)**
    - **If the inquiry pertains to Spectral interpretation assistance, the service rep will ask you to email the spectrum to: reachback@smithsdetection.com**

Support

- ***www.HazMatID.com***

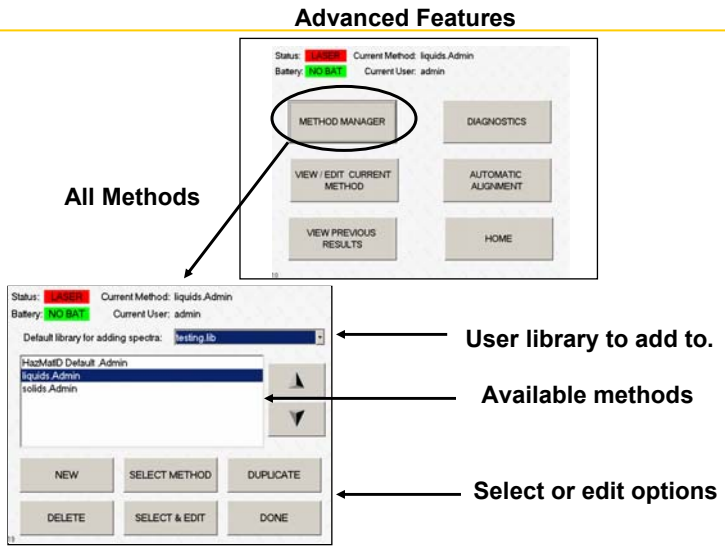
- **Web based support for up to 3 users per unit**
- **Download**
  - **User libraries**
  - **Updated Smiths/SensIR libraries and software**
- **Users forum**
- **Educational corner – FAQ**
- **ReachBack procedures**

Methods

- Methods contain all of the information the instrument needs to analyze and identify a sample
- Selecting libraries is important if new libraries are added

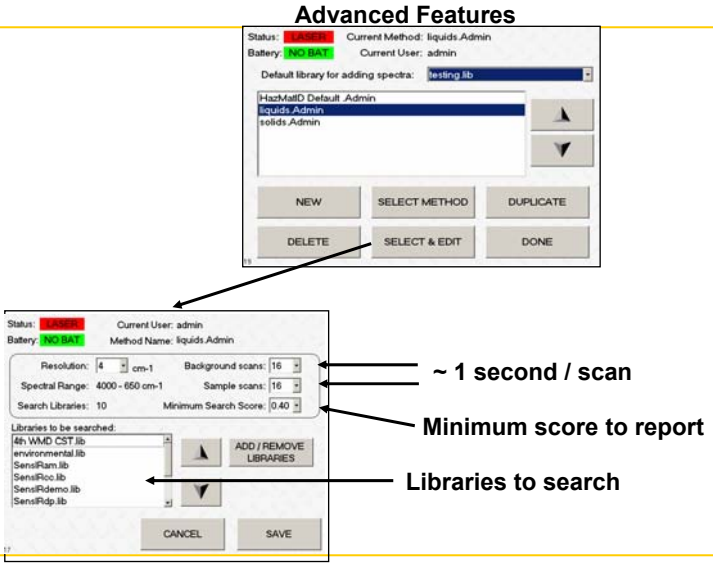
- Why edit methods?
  - Shorten measurement time
  - Reduce noise for difficult samples
  - Search different libraries
  - Display results with lower match quality (subtraction)

View/Edit Methods - HazMatID



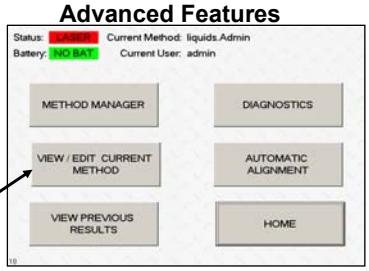
View/Edit Methods - HazMatID

Advanced Features

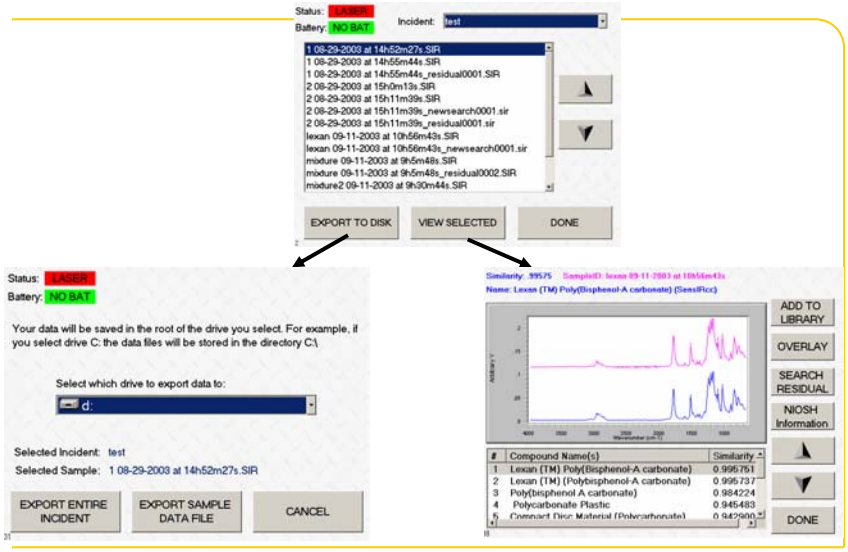


View/Edit Methods - HazMatID

Advanced Features



Previous Results - HazMatID

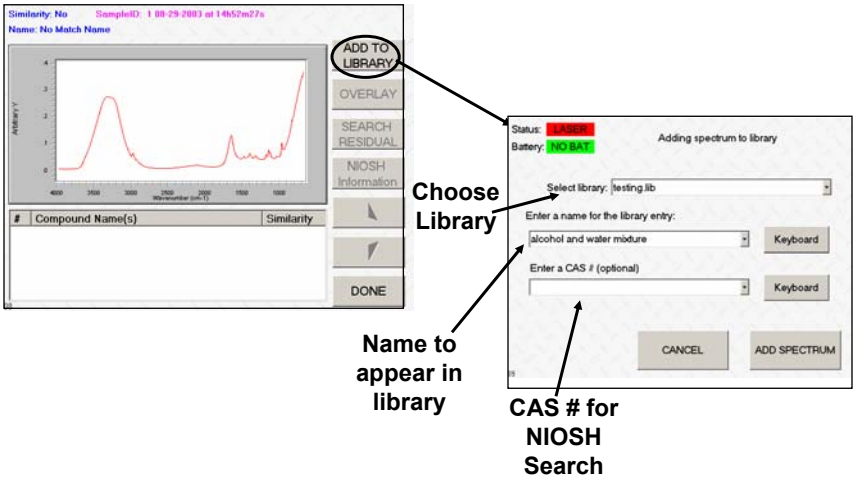


Libraries

- **Libraries contain the spectral information that is required to identify a material.**
- **Library information needs to be completely trusted as we are relying on the quality to insure quality identification.**
- **A User's library is created in the factory: "UserLibrary.lib"**
  - **All Smiths/SensIR libraries are write protected to prevent corruption.**
- **Editing/Adding libraries**
  - **Add local substances to library**
    - **Oils, fuels, maintenance materials, known chemical sites**
  - **Customize libraries for different local companies, or situations like training.**

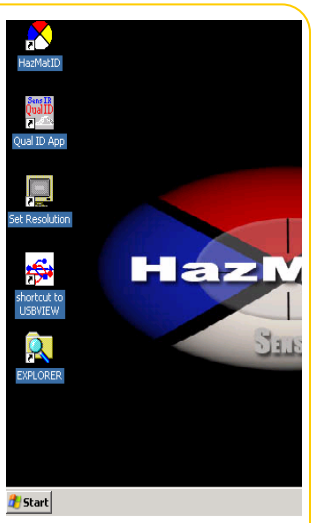
Add to Library

Data View (current or previous results)



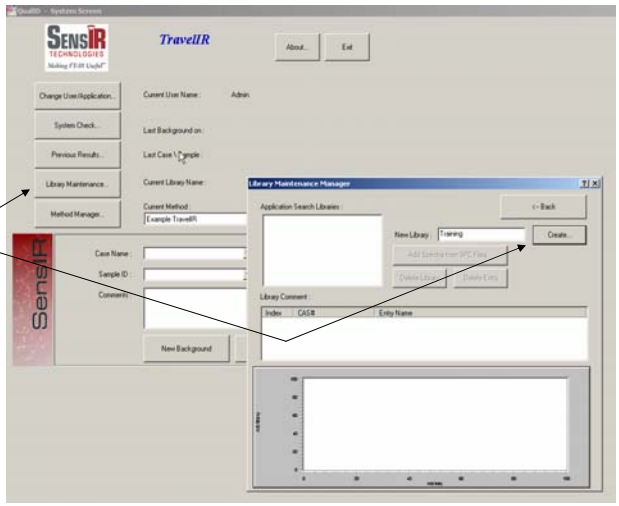
QualID Software

- **QualID software is required to create and edit Libraries**
  - **Operation of QualID is recommended for use on the system laptop.**
  - **Library maintenance allows the user to remove mistakenly added library entries.**
- **The QualID icon is located on the laptop desktop and also on the HazMatID desktop.**
  - **For operation of QualID on the HazMatID you must utilize the "Change Resolution" program also located on the HazMatID desktop. Then the QualID program can be launched.**



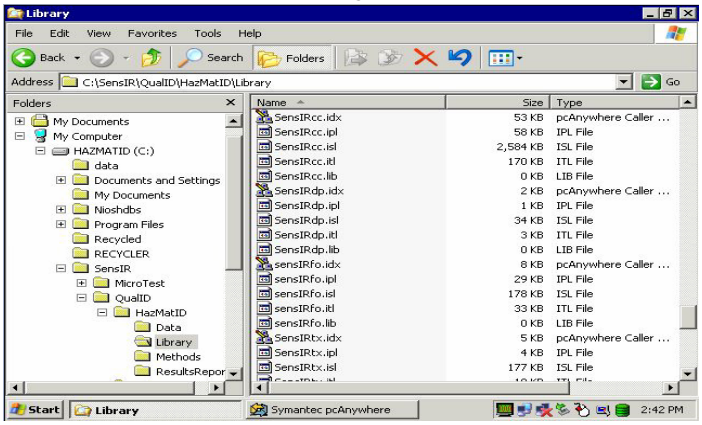
Creating new Libraries

- **Select library maintenance and type in the library name**



Copying Libraries

- **Add a known substance to the new library and then copy the five database files to the HazMatID using Flash Device or wirelessly**
- **C:\SensIR\QualID\HazMatID\Library**

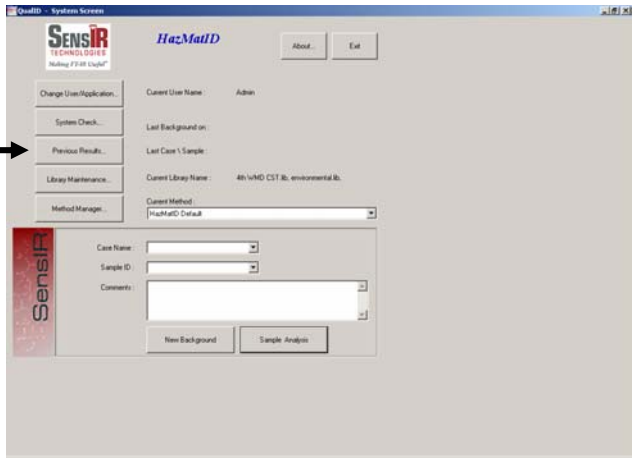


Reports

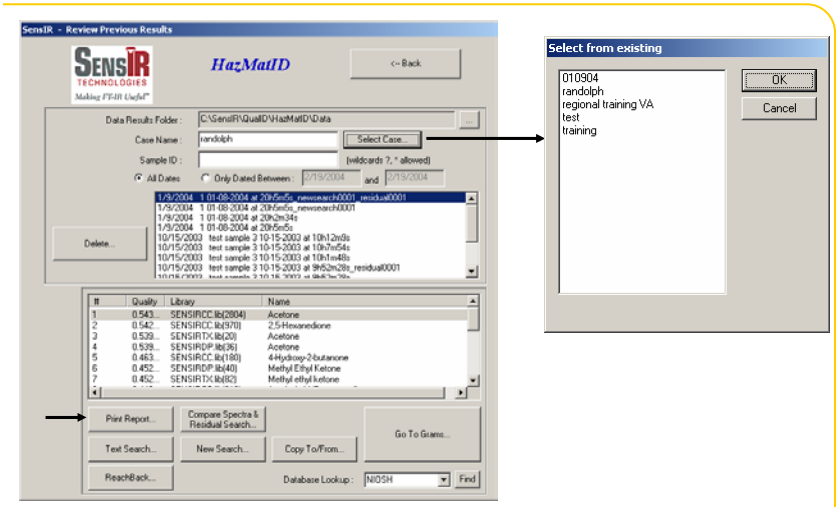
- Reports must be generated in QualID
  - Easiest to do on the Laptop
- Report Procedure
  - Transfer data files to laptop w/ PC Anywhere or Flash device
    - File location C:\SensIR\QualID\HazMatID\Data\[Incident]
    - Destination on laptop C:\SensIR\QualID\HazMatID\Data\[incident]
    - 2 files per reading – [name].spc, [name.sir]
  - On laptop, open QualID
  - Select "Previous Results"
  - Select correct case (incident) name
  - Select Print Report
    - Report printed to default printer
    - Copy saved

Reports

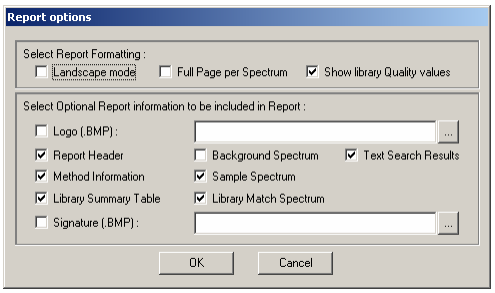
Select: Previous Results



Reports

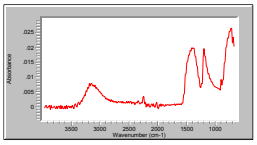


Reports

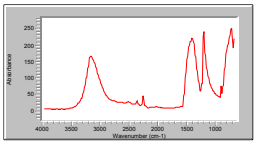


Reports

```
RESULTFILE: C:\SensIR\QualID\HazMatID\Data\training\BORIC ACID 12-17-2003 at 16h5m49s.SIR
DATE      : 12/17/03 16:07:11
METHOD    : "METHSCRATCH_TMF"
USERNAME  : ""
APPLIC    : HazMatID Application
CASE      : CANNON

BKG FILE  : CANNON\Backg.spc
DATE      : <unknown>

SAMPLE    : BORIC ACID 12-17-2003 at 16h5m49s
DATAFILE  : BORIC ACID 12-17-2003 at
16h5m49s.spc
DATE      : 12/17/03 16:07:04
```




```
LIBRARY   :
C:\SENSIR\QUALID\HAZMATID\LIBRARY\SENSIRCC.lib

BEST MATCH: Boric Acid Powder
```



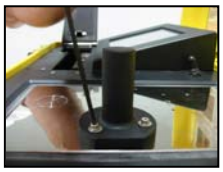
Batteries

- Battery has approx. a 2 hour service life.
  - Battery life indicator at the top of most screens.
  - Yellow warning with 30 min. remaining.
  - Do not run with less than 15 minutes remaining.
  - AC Power can be applied to replace the installed battery.
- Batteries should be stored fully charged.
  - Can remain in charger when not in use.
  - Li-Ion Batteries resist memory effects
- Do NOT store the battery in the HazMatID
  - Slow drain of the charge.
  - Battery voltage too low for the battery charger.
    - "Jump start" by inserting in the charger multiple times.
    - Move battery between the charger slots after the red light is displayed.

Maintenance

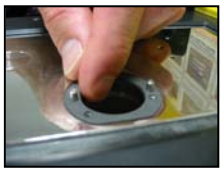
- **Alignment**
  - **Auto alignment**
    - **Anytime "Energy" is low (yellow or red)**
      15000-19999 – Yellow
      20000-32000 - Green
- **Cleaning**
  - **Washable, submersible.**
  - **Keep solvents off of case**
  - **Dry diamond before use**
- **Source Replacement**

Source Replacement, HazMatID

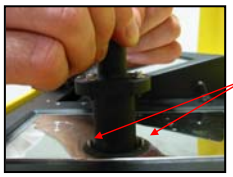


Remove old source with 3 hex bolts.

Remove plastic cover from new source.



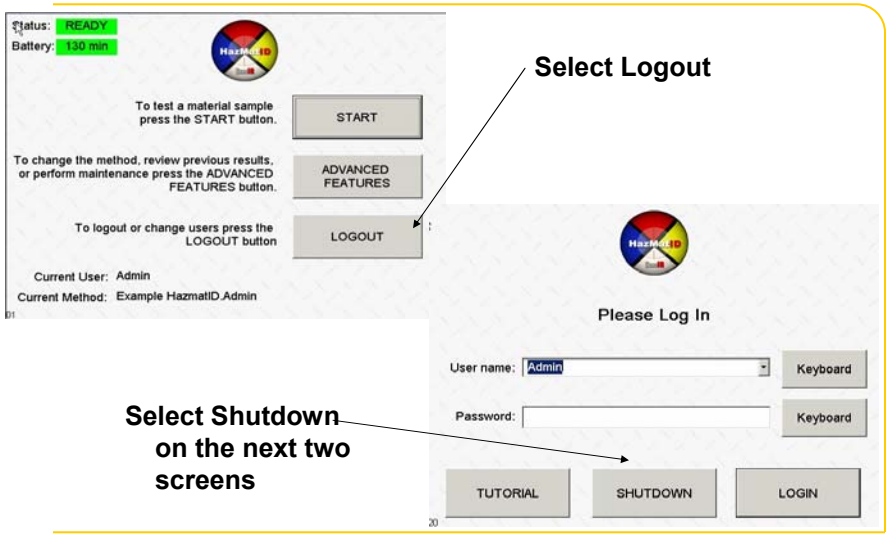
Replace source gasket And screw o-rings.



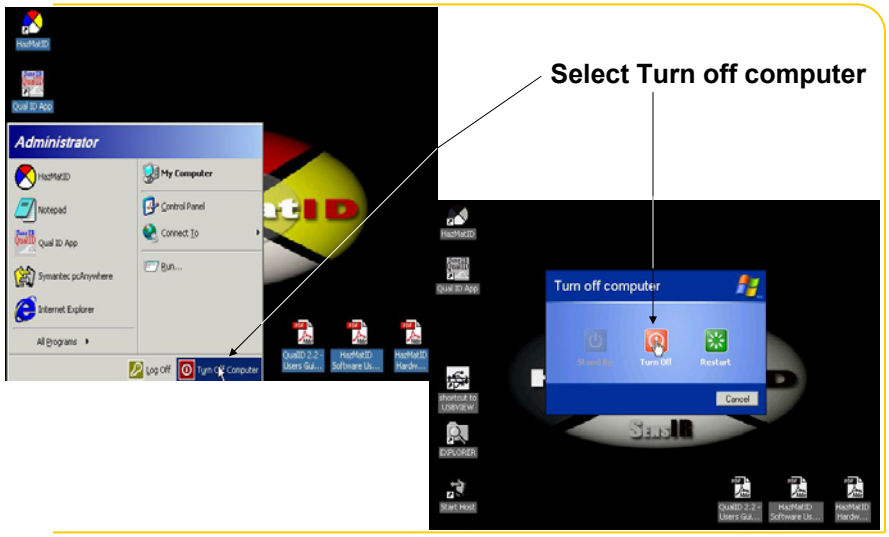
Two pins

Align new source with 2 pins and tighten 3 screws.

Powering down the HazMatID



Powering down the HazMatID



Powering down the HazMatID

- **Wait for the “safe to power off message**
- **Then flip the lever switch to 0**