HazMatID™ Chemical Identifier

Training Course:

Infrared Spectroscopy for
Hazardous Materials
Identification

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 TravelIR, 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”

- 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.

\[\text{Infrared Source} \rightarrow \text{Chemical 1} \rightarrow \text{Infrared Detector} \rightarrow \text{Spectrum} \]

\[\text{Infrared Source} \rightarrow \text{Chemical 2} \rightarrow \text{Infrared Detector} \rightarrow \text{Spectrum} \]

Infrared Radiation

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

<table>
<thead>
<tr>
<th>Wavelengths:</th>
<th>770 nm – 50 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavenumbers:</td>
<td>12,900 – 200 cm(^{-1})</td>
</tr>
</tbody>
</table>
**Infrared Spectrum of Water (H₂O)**

The infrared spectrum of water (H₂O) shows distinct peaks corresponding to different molecular vibrations.

- **Symmetric stretch** around 3300 cm⁻¹
- **Anti-symmetric stretch** around 3400 cm⁻¹
- **Bend** around 1600 cm⁻¹

**Absorbance** vs. **Wavenumber (cm⁻¹)**

**HazMatID Main Components**

- **Infrared Source**
- **Sample Press**
- **Miniature Video Camera**
- **Diamond Internal Reflection Element**
- **Battery Compartment** (battery, keyboard, USB, Network, AC plug)
- **Press**
- **Source**
- **Diamond**
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**

![Hexane infrared spectrum](image)
**Hexanol**

![Hexanol IR spectrum](image)

- **O – H stretch**
- **C – O stretch**

**Hexanal**

![Hexanal IR spectrum](image)

- **C = O stretch**

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Smiths Detection  
November 3, 2004
**Hexanoic acid**

![Diagram of Hexanoic acid]

- C = O stretch
- C – O stretch
- O – H stretch

**Hexyl amine**

![Diagram of Hexyl amine]

- C – N stretch
- N – H wag
- H – N – H bend
- N – H stretch
Aromatic (xylene)

Alcohol (C-O, OH)
Chemical bonds have absorption bands at very characteristic wavenumbers (cm⁻¹)

With practice, one can classify a chemical just by looking at its spectrum
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 HazMatID software
Molecular “Fingerprinting”

- Sample spectrum
  - Correlate
  - Library spectrum #1: $S = 0.164$
  - Library spectrum #2
  - Library spectrum #3

Molecular “Fingerprinting”

- Sample spectrum
  - Correlate
  - Library spectrum #1: $S = 0.164$
  - Library spectrum #2: $S = 0.991$
  - Library spectrum #3
Molecular “Fingerprinting”

Once the “unknown” sample spectrum is compared to all available library spectra, the results are ranked:

<table>
<thead>
<tr>
<th>Library Spectrum #</th>
<th>Correlation Value (Similarity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.991</td>
</tr>
<tr>
<td>3</td>
<td>0.773</td>
</tr>
<tr>
<td>1</td>
<td>0.164</td>
</tr>
</tbody>
</table>

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

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

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Smiths/SensIR: Libraries

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

4261 spectra

<table>
<thead>
<tr>
<th>Additional Available Libraries</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sigma-Aldrich™ ATR Library</td>
<td>18,513 spectra</td>
</tr>
<tr>
<td>Pesticide Active Ingredients</td>
<td>273 spectra</td>
</tr>
<tr>
<td>IChem™ ATR Library</td>
<td>12,706 spectra</td>
</tr>
<tr>
<td>IChem/Aldrich Combined Library</td>
<td>26,221 spectra</td>
</tr>
</tbody>
</table>
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 over 0.1
- Flat, smooth baseline
- All positive peaks

**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.

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**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

<table>
<thead>
<tr>
<th>Quality of Sample Sugar Spectrum</th>
<th>Correlation Value to Library Sugar Spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellent</td>
<td>S = .997</td>
</tr>
<tr>
<td>Poor Contact</td>
<td>S = .989</td>
</tr>
<tr>
<td>Bad Baseline</td>
<td>S = .797</td>
</tr>
<tr>
<td>Negative Peaks</td>
<td>S = .750</td>
</tr>
</tbody>
</table>

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

### HazMatID Advanced Topics

**POP QUIZ**
**Good or Bad?**

**BAD!**
- Absorbance values too low

*Cover diamond, Apply more pressure*

**Good or Bad?**

**GOOD!**
- Absorbance over 0.1
- Good signal-to-noise
- Flat baseline

*Wavenumber (cm⁻¹)*

*Absorbance*
Good or Bad?

Record New Background

Sloping baseline

Wavenumber (cm⁻¹)

Absorbance

4000 3500 3000 2500 2000 1500 1000

BAD!

Good or Bad?

Negative peaks

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

![Diagram showing mixture comparison and similarity score]

High similarity
**HazMatID - Mixture Example**

**Mixture not in library**

Main component matched but with low similarity

<table>
<thead>
<tr>
<th>Compound Name(s)</th>
<th>Similarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose acid</td>
<td>0.903779</td>
</tr>
<tr>
<td>Water</td>
<td>0.851920</td>
</tr>
<tr>
<td>Betadine (TM) Antisepctic Solution</td>
<td>0.851681</td>
</tr>
<tr>
<td>Distilled Water</td>
<td>0.844776</td>
</tr>
<tr>
<td>Astronin 1R</td>
<td>0.837781</td>
</tr>
</tbody>
</table>

**HazMatID: Mixture Example – 50/50 Water, Ethanol**

Shape of water seen in sample

Water in top 5 hits

<table>
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</tr>
<tr>
<td>Astronin 1R</td>
<td>0.837781</td>
</tr>
</tbody>
</table>

Sample has more peaks than water
**HazMatID: Mixture Example – 50/50 Water, Ethanol**

Automatic Result

**HazMatID: Mixture Example**

Visual compare needed to confirm

Top 10 hits shown after "Save".

Similarity low after subtraction
**HazMatID**: Mixture Example – 90/10 Water, Ethanol

Only small difference noted

<table>
<thead>
<tr>
<th>#</th>
<th>Compound Name(s)</th>
<th>Similarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Distilled Water</td>
<td>0.999569</td>
</tr>
<tr>
<td>2</td>
<td>Water</td>
<td>0.997059</td>
</tr>
<tr>
<td>3</td>
<td>Betadine (TM) Antiseptic Solution</td>
<td>0.998713</td>
</tr>
<tr>
<td>4</td>
<td>Actomid III</td>
<td>0.990774</td>
</tr>
<tr>
<td>5</td>
<td>Rubbing Alcohol (80% Isopropyl, 5%)</td>
<td>0.994868</td>
</tr>
</tbody>
</table>

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?
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.
**Bacteria Components**

![Graph showing components of bacteria components: Protein, Lipid, Carbohydrate]

**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 Diagram](image)

**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
**HazmatID**

- **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

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**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](http://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)

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**View/Edit Methods - HazMatID**

**Advanced Features**

**All Methods**

- User library to add to.
- Available methods
- Select or edit options
**View/Edit Methods - HazMatID**

**Advanced Features**

- ~1 second / scan
- Minimum score to report
- Libraries to search

**Shortcut to current method**
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)

- Choose Library
- Name to appear in library
- CAS # for NIOSH Search

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**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:\SensiIR\QualID\HazMatID\Data\[Incident]
  - Destination on laptop
    C:\SensiIR\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

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_TMP"
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.
- Align new source with 2 pins and tighten 3 screws.
Powering down the HazMatID

Select Logout

Select Shutdown on the next two screens

Select Turn off computer
Powering down the HazMatID

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