



Classification and Identification of Hazardous Chemicals

The Role of Spectroscopic Analyzers

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Overview

In the ancient Indian parable, six blind men feel a single, separate part of an elephant and thus describe the whole animal in six widely disparate ways. The moral is that we sometimes have a tendency to believe a result based on our limited, subjective experience. The purpose of this article is to advocate for the need to use all the tools available to identify and mitigate a potentially hazardous incident, and to use them in the most logical manner to reduce risk. In that manner, the “elephant” will be properly described.

The critically important job that Hazmat first responders undertake everyday requires that they neither trust one data point to reach a conclusion, nor should they bias their conclusion by how the investigation is undertaken. Fortunately, responders have a rich toolbox of methods and technologies at their disposal to provide more complete information on an incident. Nevertheless, time is of the essence and that often conflicts with the need to acquire as much information as possible. When the need to gather data to reach a conclusion is prejudiced by lack of time, one may be forced to make a decision based on a limited view of the hazard. This, of course, increases the risk of the hazard to the safety of the community as well as the responder’s personal safety.

Twenty years ago, the first spectroscopy-based field analyzers were introduced to the hazmat responder community by SensIR Technologies and Smiths Detection. This technology allowed responders to rapidly obtain information on the identity of a chemical hazard, enabling a faster response. These systems used Fourier transform infrared spectroscopy (FTIR) and were well-suited to analysis of solid and liquid unidentified. Later, hand-held analyzers based on Raman spectroscopy were introduced from a number of companies and became widely accepted. Today, there are numerous FTIR and Raman spectroscopy-based analyzers in operation throughout the world identifying TICs, white powders, explosives, CWAs and other unidentified hazardous materials. These tools allowed responders to go from a presumptive analysis to actual identification

These tools are of substantial value and provide an important data point in the quest for characterizing and identifying an unidentified substance. On the other hand, reliance on a single data point to provide the correct answer leads us back to the elephant problem. NFPA 472 [ref. 1] recommends hazmat teams use a “Risk Based Response” approach for hazardous materials/WMD incidents and SWGDRUG (Scientific Working Group for the Analysis of Seized Drugs) recommend a multi-faced approach, ASTM E2329-17 [ref. 2]. These systemic

approaches are based upon the facts, science, and circumstances of the incident. To increase confidence and reduce risk, all information needs to be considered:

1. **Classification Kit** - following the protocol for use, are you confident that the hazardous material is fully characterized?
2. **Meters**. Such as combustible gas indicators (CGI), photo ionization detectors (PID)
3. **Chemical Analyzers**, both FTIR and Raman instruments available? If so, are the identifications confirmatory? If only one instrument is available, how do you process the results to enhance and justify your confidence in the answer? How do you mitigate risk caused by too much faith in “red-green” answers?
4. **Experience and common sense**. Are the results from the instruments consistent with results from your classification kit? From what you learn about the incident, the location, and physical environment, is the identification of the hazard logical?

A Practical Approach to Chemical Classification and Identification

We too advocate using a systematic process to analyze a situation in which the optimum response is based on the facts, science and circumstances of the incident. There are 4 main categories to this systematic approach that are considered:

- Isolation distance from the hazard, which is based on the physical phase of the unknown (solid, liquid or gas). These distances are designed to get or keep the public out of harm's way.
- The personal protection equipment required to keep the responder safe.
- The equipment required to minimally classify and hopefully identify the unknown material.
- What is necessary to decontaminate the area.

There should be a logical progression of steps taken to classify the chemical nature of an unidentified material, as well as how to understand these substances may act in an incident.

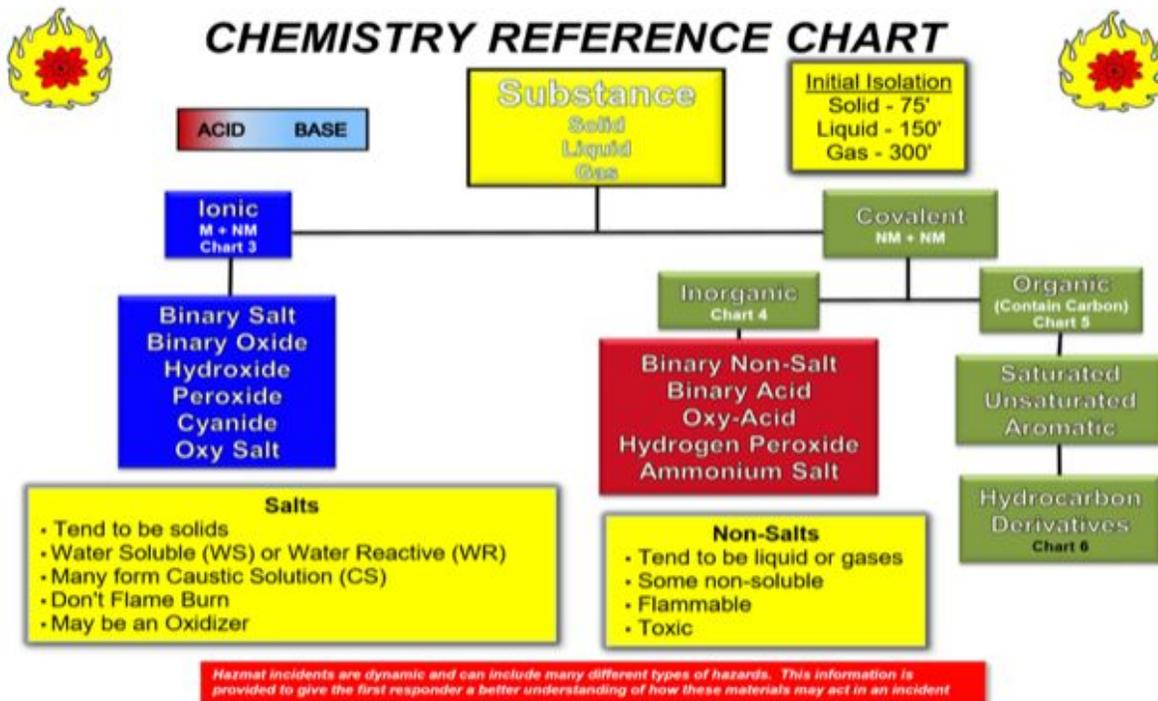


Image above: general overview of potential chemical hazards and major properties

An initial step is to determine if the material has ionic or covalent bonds. In the former case, we are describing what are typically salt-type materials and these can be metal or nonmetallic salts. For example, the common algicide copper sulfate is an ionic salt that contains a metal atom. Ammonium chloride is another ionic salt, which does not contain a metal atom. In both cases, and in the case of many ionic compounds, they are soluble (or reactive) in polar solvents such as water. In simple ionic compounds, the parts of the overall molecule are held together by weak forces and thus easily dissolve in the correct solvent. There are more complex, types of salts that are ionic but also contain a cation and an anion that is covalently bonded (e.g., hydroxide, peroxide, cyanide, and oxy-salts). On the other hand, molecules containing only covalent bonds are more strongly bonded and will not typically dissolve or be miscible in polar solvents. Thus, solubility of solids in water or miscibility of liquids in water can give us a first important clue to classifying the material. If a substance dissolves in water, often it is a salt. If a liquid substance floats or sinks in water, it is often a covalently bonded organic or inorganic compound. If an unidentified liquid forms immiscible layers with water, it is likely a hydrocarbon and the density of the liquid relative to water defines whether it sinks (carbon

tetrachloride) or floats (gasoline) on water. If an organic compound is miscible with water (dissolves) it is likely a low carbon chain molecule, perhaps containing polar groups such as an alcohol. Simple tests and observations can provide important clues for classifying unidentified solids and liquids.

Tools for Classifying Unidentified Substances

Among the most useful and least expensive tools for classifying an unidentified chemical are the indicator paper strips. We advocate the use of these as a front-line mode of analysis regardless of what electronic equipment is available. The main indicating papers are:

- Water paper – determine the presence of water
- pH paper – is the substance acidic or basic
- starch-iodide paper – is the substance an oxidizer (e.g., peroxide, nitrate)
- fluoride paper – to detect the presence of toxic fluoride ion
- M-8 paper – detect CWA.

Responders are taught in technician classes to use multiple reference materials for facts about the chemical(s) they are dealing with. Sometimes negative results are just as confirming as a positive response. An example might be a response to an incident involving acetone. There would be no response for the water, pH, KI, and F papers whereas M-8 paper would exhibit a red color change.

These strips can be conveniently carried and used via a method (“bear claw”) in which one of each of the individual strips are attached to a central adhesive strip. In that manner, all of the testing strips are at hand, ready for use.

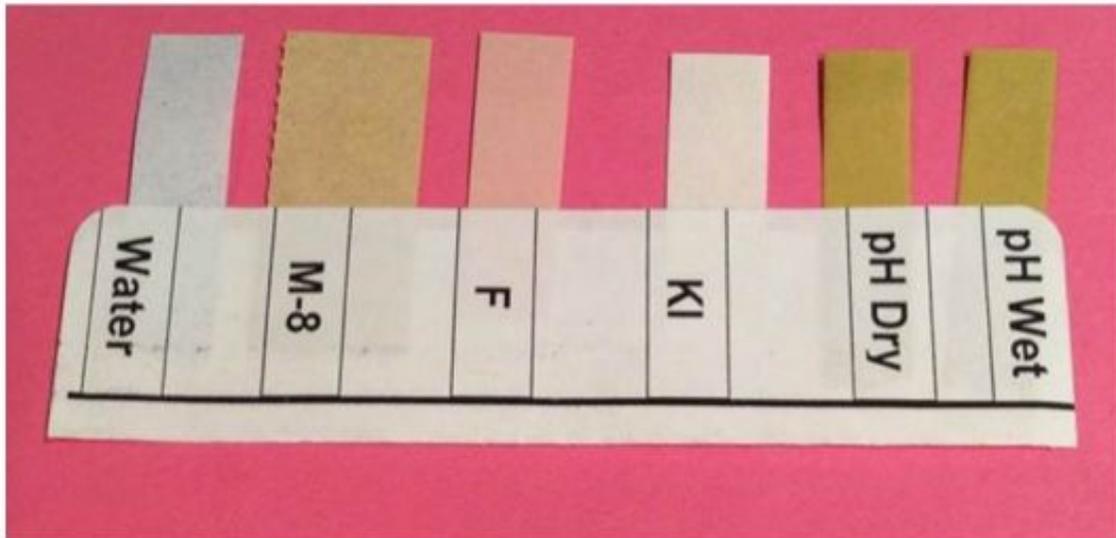


Image above: "Bear Claw" - A convenient means for carrying and using the important indicator paper strips

The most commonly used electronic devices are metering devices, which are used for classifying gases, vapors and liquid unknowns. Most liquids have some vapor pressure, which is defined by the amount of vapor present at atmospheric pressures and temperatures. Highly volatile liquids like acetone or ether have higher vapor pressures whereas the CWA VX has a nearly negligible vapor pressure, but it is present. Another important factor is vapor density, which is the weight of the vapor in relation to air. Some gases (only 13) have less vapor density than air (hydrogen, ammonia, helium, acetylene, methane, natural gas, neon) but others are heavier than air (carbon dioxide, propane) and may create a suffocation risk. A critical parameter is flashpoint which is the minimum temperature of a liquid where enough vapor is produced that an ignitable mixture can result. Flashpoint is the primary factor in determining whether a liquid is likely to create fire hazard. Also critical is the flammable range which is the vapor concentration in air where combustion must occur. Materials that have a wide flammable range are the most hazardous.

The main instruments for measuring vapors are photoionization detectors (PID) and multi-gas detectors. These devices produce measurements of atmospheric hazards and provide the responder with information regarding the need for personal respiratory protection. PID are useful because they respond rapidly and are sensitive to volatile organics. PIDs are not specific and the concentration they measure may reflect a number of different vapors with varying

concentrations. They also cannot measure substances with ionization potential's (IP) greater than the energy of the lamp, usually 10.6 eV.

Multi-gas detectors are easy-to-use and have sensors for combustible gas, oxygen, carbon monoxide, and hydrogen sulfide and have built in warnings to alert for these gases. They provide measurement of non-compound specific lower explosive limit (LEL) for combustible gases.

Tools for Identifying Unknown Substances - FTIR and Raman analyzers

Currently, there are many FTIR and Raman analyzers involved in Hazmat applications, world-wide. Though both techniques fundamentally reflect the molecular bonding of a compound, the physics behind the techniques are quite different and each method has its own strengths and weaknesses.

FTIR and Raman Spectroscopy – the Basics

FTIR Spectroscopy is a molecular spectroscopy technique that probes the interaction of mid-infrared (wavelengths of approximately 2.5 microns to 15 microns) energy with matter. The information provided by FTIR spectroscopy results from absorption of light by molecules in a sample. FTIR spectroscopy provides information about the absolute frequencies at which a sample absorbs infrared energy. This results in a characteristic spectrum which is a fingerprint of the structure of molecules in a sample. For a molecule to be infrared active, one or more bonds must undergo a change in dipole moment, which is the difference in electric charge between atoms that occurs when IR radiation is absorbed.

Raman Spectroscopy is also a molecular spectroscopy technique that probes the interaction of light with matter. In this case, the light comes from a laser, which in most handheld analyzers, typically operates at the red end of the visible spectrum (wavelengths of 0.75 microns to 1.05 microns). The information provided by Raman spectroscopy results from scattering of light from molecules in a sample. Raman spectroscopy of a compound provides a spectrum characteristic of the relative frequencies at which the sample scatters light. For a molecule to be Raman active, one or more bonds must undergo a change in polarizability, which reflects how easy it is to distort the electron cloud around a molecule when it interacts with light.

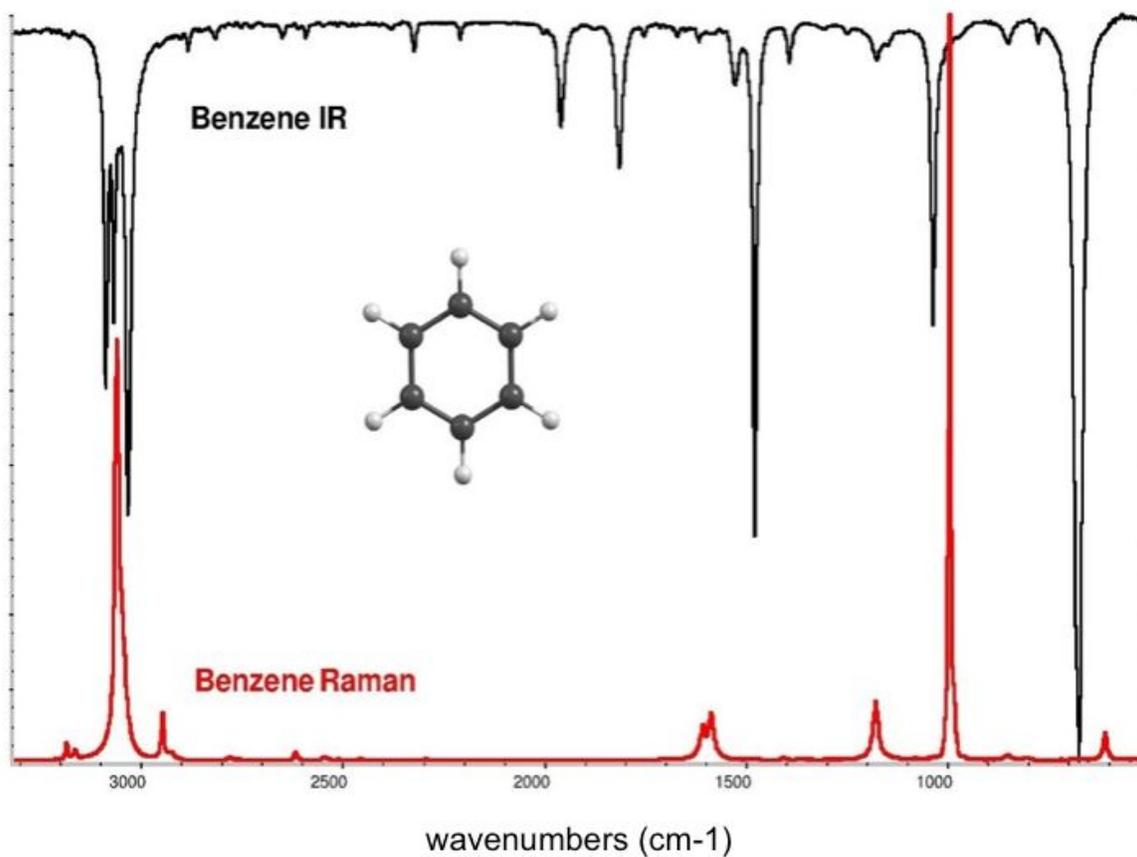


Image above: IR transmission (black) and Raman scattering (red) spectrum of benzene illustrating complementary nature of the two molecular spectroscopy techniques [ref.3] for this symmetric molecule.

	Frequency (cm^{-1})	IR ^a	Raman ^b
Alkanes			
CH ₃ sym stretch	2862–2882	vs	vs
C—C stretch	1040–1100	—	s
Cyclopentane ring breathing	889	—	s
Alcohol O—H stretch	3635–3644	m	w
Acetylene C—H bend	825–640	s	w
Acetylene C≡C	2230–2237	—	s
C≡N stretch in R—CN	2230–2250	s	vs
Cyanate C≡N	2245–2256	s	vs
C—H in R—CHO	2800–2850	m	—
C=O in R—CHO	1730–1740	vs	w
R—NO ₂ asym stretch	1530–1600	vs	m–w
R—NO ₂ sym stretch	1310–1397	s	vs
C—S stretch	580–704	—	vs
S—H stretch	2560–2590	w	s
R ₂ S ₂ S—S stretch	507–512	m–w	s
Benzene ring breathing	992	—	vs
Primary R—Cl	650–660	s	s
Primary R—Br	565–560	s	vs
Primary R—I	500–510	s	vs

Image above: Examples of IR and Raman band assignments with relative strengths. vs=very strong, s=strong, m=medium, w=weak, dash=no band [ref. 4]. This illustrates the complementary nature of these two molecular spectroscopic methods and why, when possible, using both technologies provides the highest level of confidence in identifying a suspect material.

Both FTIR and Raman spectroscopy provide information about the identity of a substance. In both cases, a characteristic pattern of bands (spectrum) is formed and the position and intensity of the spectral peaks reflect the molecular structure and composition of the substance. Spectral libraries of known compounds are used as a reference database, and the identity of unknown compound or mixture is revealed by a search algorithm that provides the best match of the spectrum of the unidentified substance with a reference spectrum. Along with the identity of the substance, the search algorithms provide a numerical representation about the quality of the match. The higher the numerical match, the better the likelihood of correct identification. However, because of the fundamental difference in the physics of how each technique

operates, the pattern of bands that are formed are very different for the FTIR and Raman methods, and each requires their own separate reference library. As a result of the difference in these fundamental principles of operation, FTIR and Raman are considered complementary techniques. This provides a great advantage to the hazmat responder with respect to learning the identity of a substance.

Spectroscopic Analyzers – Gaining Confidence in an identification

If one has access to both FTIR and Raman analyzers, and both give the same result for an unidentified substance, and the answer is consistent with initial chemical classification methods, the confidence in clearing an incident or understanding what needs to be done to remediate a site is very high. What if one spectroscopic method provides an answer that is associated with a high confidence match but the other does not? This can be very useful, as well, and this is again related to the fundamental difference in physics of how the two techniques operate.

Sometimes it's the wavelength range of the instrumentation that affects the spectral match quality. For example, if there is an incident with a yellow powder present, and the Raman gives a strong spectrum and a high-quality match for sulfur, but the FTIR provides no information, you can have high confidence that the substance is sulfur. That is because the Raman active modes of sulfur (and IR) are at a low frequency, observable by Raman hazmat analyzers but not by typical FTIR hazmat analyzers. What if a white powder is found that dissolves in water and there is no information provided by either spectroscopic technique? Since it dissolves in water, it is clearly an ionic salt and since there is no molecular spectrum, it is a simple ionic compound, perhaps sodium chloride or sodium fluoride, which can be further substantiated by standard classification testing with indicator papers. Some molecular vibrations are IR active and Raman inactive, and vice versa. Some bonds, like the O-H stretching vibration, are very strong in the IR, but very weak in the Raman spectrum. If a liquid that gives no Raman spectrum, but a very strong IR spectrum that matches the reference spectrum for water, confidence can be very high in the identification (confirm with water indicator paper). The bottom line is that both positive and negative matches can be informative, assuming you use all the tools, logic and evidence available.

With respect to mixtures, commercially available hazmat analyzers contain algorithms that can mathematically separate and identify components of mixtures. For example, with a residual search algorithm, the spectrum of an unidentified sample is matched to that of known compounds in the on-board database, and the primary component of the mixture is determined. An automatic subtraction of the library reference spectrum from the unidentified substance's

primary component spectrum is then executed, and if any residual peaks remain, they are searched against the database to identify secondary, lower level compounds that may be present.





Images above: Mixture Analysis Example: The best match for the spectrum of this white powder (top) is found to be fructose, but overlaying the spectrum of the unidentified substance with the fructose spectrum, clearly shows that there are other bands are present. Expanding the key spectral region (middle) provides more detail. What do they arise from? Using an automated residual search algorithm, which subtracts the fructose reference spectrum from that of the unidentified white powder spectrum, the remaining bands are again searched and found to arise from a secondary component, caffeine.

Relative Strengths and Weaknesses of FTIR and Raman Spectroscopy for Hazmat Identification

Raman spectroscopy has two advantages that can have value to hazmat responders. Whereas water exhibits a weak Raman effect, it is a strong absorber of mid-infrared radiation. This means that water is “transparent” to Raman spectroscopy, whereas it is “opaque” in FTIR spectroscopy. Thus, identifying solutes in aqueous solutions is easier to accomplish with Raman spectroscopy. Another advantage that Raman enjoys is that spectra can be recorded directly through plastic bags or glass containers and therefore substances can be analyzed without opening a container, thus reducing potential exposure to the operator. Both of these advantages have pitfalls however. In the case of measuring solutes in water, one must remember that the Raman effect is very weak and thus is not particularly analytically sensitive. It is difficult to measure unidentified solutes in water if the substance is present below 5%. As far as measuring through plastic bags or glass bottles, this can be affected by fluorescence either by the container or the substance in the container. Often at an incident, the unidentified substance is not in a transparent container (or any container), so the advantage is not relevant.

Furthermore, fluorescence is a far stronger effect than Raman scattering and will swamp the Raman signal. Typical handheld Raman analyzers operate at wavelengths towards the red end of the visible spectrum in order to minimize fluorescence, however the further into these longer wavelengths, the weaker the Raman signal so higher laser energies are typically used. Dark colored substances can absorb the laser energy and decompose. To get good quality Raman spectra from colored substances often means increasing the laser power, which increases the likelihood of sample decomposition, or even ignition. Raman spectroscopy is effective at measuring bonds that are easily polarized when interrogated by light energy such as C-C, N=N, O-O, etc.

FTIR spectroscopy has significant advantages in many situations. It is a far stronger technique than the Raman effect and thus it is inherently more sensitive with respect to levels of substances that can be analyzed. This is quite important when considering mixture analysis. It also means that very little sample is required to get an excellent spectrum, which yields accurate library searches and higher confidence identification. Typically recording an effective FTIR spectrum requires less than 30 seconds. Moreover, the IR database libraries are far more extensive than those for Raman spectroscopy. The mid-infrared region that FTIR spectrometers operate is called the “fingerprint region” of the spectrum. Peaks in the mid-infrared can be directly assigned to fundamental molecular vibrations, and this means that functional group charts can be automatically displayed with the spectrum to give the operator an indication of the specific bonds present in the unidentified material. This, in turn, results in a higher level of confidence in the results of a search. Since FTIR spectroscopy measures molecules with strong dipole moments, molecules common functional groups such as C=O, O-H, N=O etc. yield high quality spectra. Fluorescence is not an issue in the mid-infrared regions that FTIR operates in, and the color of the compound does not affect the ability to record spectra. In FTIR spectroscopy, the amount of energy deposited on the sample in order to get a high-quality result is so low that there is no danger of sample decomposition or ignition.

The importance of Ergonomics

The original HazmatID was a case mounted FTIR system that weighed about 12 kgs. Today, all currently available FTIR and Raman systems for hazmat are hand-held and weigh as little as 2 kgs. There are positives to these handheld systems, mostly associated with their size and convenience. When in gear, their light weight makes them easier to carry and they take up less room on a rig. There is downside to small size as, as well, mostly associated with usability. Handheld systems have small display screens that can be hard to read and have small touch-sensitive buttons that may be difficult to activate while in gear, and may not operate at all with certain glove materials. Many responders who have used both handheld and

case-mounted systems prefer the latter and regret that they are no longer available, since the displays are far easier to read and system control is easier. Furthermore, a larger display screen makes it easier to expand and zoom various spectral regions. Though green-red alerts are useful, there is not much information provided to back-up the rationale for the result. That information derives from the spectra, and the ability to easily visualize and manipulate spectra can be very valuable in building confidence in a result. This is far easier to accomplish with a larger display screen.

There is some awkwardness in sample analysis using handheld systems that should be considered, especially when in gear. For example, many handheld systems require the user to bend down and touch the system sensor to the liquid or solid substance. Trying to analyze a sample in this manner while in gear and at the same time trying to manipulate small touch sensitive buttons on the display can be difficult. Also, these devices are not intrinsically safe and can pose added hazards, since most common hazard class of material releases are flammable liquids. For Raman analyzers, one way to get around this problem is to place some of the unidentified substance in a small glass vial for analysis, however, this adds another potentially problematic step in the analysis process.



Images above: note that the display screen and the sample sensor (at the bottom of the analyzer) are in the same physical plane, making the act of touching the sample to the unknown substance while manipulating controls and observing the results on the screen difficult. These actions are further complicated by the physical act of kneeling or bending while in gear. Ergonomics are important. [photos from ref. 5,6]

Another issue to consider when deciding whether a handheld or case-mounted system best meets requirements is that the size advantage that handhelds enjoy also makes them easier to

accidentally drop, or even to misplace. Handheld devices may also require peripheral equipment such as modems, laptop computer, etc.

A modern, light, case-mounted system with large display screen and stable sample analysis platform can have substantial ergonomic advantages and may be a better choice depending on the team's requirements.

What functions should an analyzer provide?

In the ideal world, a team would own both FTIR and Raman systems, and many larger teams are fortunate to have both technologies available. The choice of which technique is better suited to a team's need is going to be dependent on a number of factors including the type of industries or research centers in a team's area of responsibility, the type of substances that may be encountered, the comfort level of the operators with particular technology, the cost factor associated with acquiring and maintaining a sophisticated analyzer system and the comfort level with the manufacturer of the analyzer with respect to technical support and reputation.

As far as the analyzer system itself, here are some questions to consider:

Ease of use

- Is the software easy to understand and intuitive?
- Are the analyzer's functions and capabilities easy to access?
- How easy is to communicate results to other team members?
- How easy is it to perform detailed inspection of spectra, for example using spectra expand and zoom features?
- How easy is it to physically measure samples?
- How easy is the sensor to clean?
- Is the system easy to decontaminate?

Performance

- How quickly does the analyzer stabilize after being turned on?
- Does the analyzer have mixture analysis capability?
- Does the software provide functional group assignments to make identification easier?

- Are extensive spectral libraries available?
- Can you download into the spectral library other analyzer spectra (e.g., HazmatID files)
- How is data from previous incidents archived and how quickly can it be retrieved.
- How easy is it to communicate results via Bluetooth or e-mail. How effectively do they work?
- Is the analyzer designed to be equally effective in both warm zone/hot zone?
- How easy is it to download reference material from other sources?
- Is the battery hot swappable and compatible with other analyzers?

Ergonomics

- Are the alphanumeric characters on the display easy to read?
- How easy is it to use the controls via hard keys, touch-sensitive buttons while in gear
- How readable is the display in variable ambient light?
- Does the analyzer's haptic display respond effectively to all types of glove materials
- Is the form factor of the analyzer consistent with easy sample analysis

Ensuring that the Analyzer Fits Your Team's Needs

Because of the complementary nature of the information that FTIR and Raman chemical analyzers provide, ideally a hazmat team would own both types of systems, and many larger teams actually do have access to both. However, financial realities may make this unlikely or impossible for many other hazmat teams. Therefore, a number of decisions need to be made when a team decides to acquire their first spectroscopic chemical identifier, or to replace an older system. Is Raman or FTIR technology a better choice for that team? Is a handheld or a case-mounted system preferable? What is the reputation of the manufacturer and how committed are they to the hazmat community? Does the level of technical support that the manufacturer offers meet the team's requirements? What is the initial cost of the system and longer-term operational costs such as maintenance contracts?

The best way to find out this information, and to determine how well an analyzer functions is through live, in-depth testing. This is often done one-on-one at site that the team selects, or at local and regional meetings where many manufacturers bring their equipment.

Ideally, the best way to evaluate an analyzer is to have the manufacturer provide a system to the team for a few days and have a trained hazmat responder use it in the field. This approach

may be effective, but also presents logistical and technical problems. A more practical approach is to have a demonstration of the system at the team's headquarters on samples that the hazmat team provides. In this manner more team members can try the system and determine comparative usability and performance. A less useful way to test a system is for the manufacturer's representative to run the system using samples that he or she provides. Getting good results on pure white powders or clear liquids contained in a small glass vials is straightforward, but does not reflect the nature of the samples that the hazmat team will likely face. Turbid samples, colored samples, multilayer liquid samples, and mixtures are the challenging samples that reflect real-world situations. These will challenge the optical performance of the system, its usability and effectiveness of the algorithms to identify the substance.

Summary

Today's hazmat teams are fortunate to have a suite of methodologies at their disposal for both classification and, more recently, identification of hazardous chemicals. We advocate a science-based approach to determine the identity of a substance that utilizes these tools in a systematic manner. Simple chemical tests and substance-specific indicator papers give important insight into the classification of the unidentified substance. FTIR and Raman spectroscopic analyzers provide another dimension since they can specifically identify potentially hazardous substances and provide supporting information to clear and remediate an incident. When used in conjunction, the collective results provided by these tools provide the responder with the highest degree of confidence for mitigating an incident.

References

- [1] National Fire Protection Association, "Standard for Competence of Responders to Hazardous Materials/Weapons of Mass Destruction Incidents"
- [2] ASTM E2329-17, "Standard Practice for Identification of Seized Drugs"
- [3] image appears on Wikimedia Commons, "Spettri Raman ed IR del benzene.pdf"
- [4] McCreery, R.L., Raman Spectroscopy for Chemical Analysis, 3rd Ed., Wiley, New York, 2000
- [5] from <https://www.epequip.com/catalogue/all-hazards-management/hazmatid-elite/>
- [6] from <http://www.warsash.com.au/HAZMAT-chemical-id/>