Combining Infrared and Raman Spectroscopy on a Single Platform to Identify Unknown Chemical Hazards

Application Brief AB-076

Motivation

While a common premise to all emergency response plans is the accumulation of reliable, accurate, and timely information, no single portable device can identify all hazardous chemicals with 100% confidence. Consequently, emergency responders are constantly adopting multiple tools to detect and identify unknown hazardous chemicals. The devices available are designed for a variety of applications yet require the user to manually integrate the data into their response decision as recommended by the National Fire Protection Association, document NFPA 472, *Standard for Professional Competence of Responders to Hazardous Materials Incidents.*[1] Although no two events are exactly alike, a response plan with systematic practices can be valuable, particularly in the context of the strict laboratory standards exercised within the scientific community. Indeed, the National Institute of Standards and Technology (NIST) advocates the use of multiple data sources to not only characterize and identify unknowns, but also to assure the validity of the results.[2] For emergency responders, however, these principles are difficult to uphold since key decisions need to be made outside of the laboratory setting very quickly.

Additionally, the technology is growing more-and-more sophisticated making it difficult to understand the advantages and limitations of each device. In an effort to minimize these difficulties Smiths Detection is developing and providing emergency response teams with a reliable, quick, and systematic suite of portable instrumentation that can be used in combination, and that adheres to the practices adopted in the responder's plan of action.

To identify solid and liquid chemical hazards, Smiths Detection offers the HazMatID™ and RespondeR RCI™. The HazMatID relies on infrared (IR) vibrational spectroscopy and has been widely accepted by responders over the past 5 years. The RespondeR uses Raman vibrational spectroscopy (a laser-based technique) to offer rapid analysis that is complimentary to the information the HazMatID provides, in addition to resolving the primary limitation of IR technology – aqueous solutions. Although both of these instruments identify unknowns by gathering information about the molecule's vibrating chemical bonds, the devices are unique because they utilize different technologies to obtain the chemical identity. Within the scientific community infrared and Raman are proven techniques, meaning that the information obtained from each can be combined to more thoroughly analyze a unknown chemical. For all of these reasons, Smiths Detection has implemented innovative software that unites the complimentary information via wireless Bluetooth™ communication to perform the advanced analysis.

Combined analysis on a single platform

Used independently, the HazMatID and RespondeR identify solid and liquid unknowns by matching a measured spectrum to an extensive database of known chemicals. This process is comparable to human fingerprint identification, where the sample spectrum can be viewed as a "fingerprint" of the molecule. Indeed, both of the portable instruments are easy-to-use in form and function, and provide the similar touchscreen interface software. What Smiths Detection offers, when infrared and Raman technologies are used in combination, is the power to provide more thorough analysis using advanced, customized software. By automatically integrating the complimentary data on a single platform, the emergency responder now has the ability to validate hazardous chemical identifications using multiple data sources and therefore make critical decisions

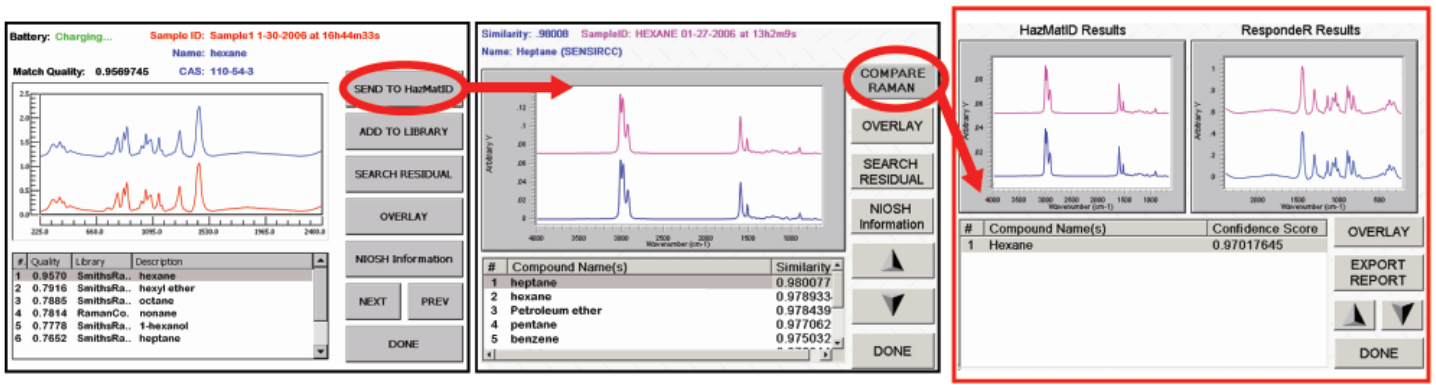

Figure 1. Systematic sequence of analysis using the RespondeR and HazMatID in combination to identify an unknown sample with much greater accuracy (example = hexane).

with greater confidence. Specifically, the library search results of the RespondeR are transmitted to the HazMatID instrument via Bluetooth™ technology within seconds, where the Raman data is stored. The same unknown sample can then be independently analyzed on the infrared diamond sensor, and then compared with the Raman data using the new, statistically-based software available for the HazMatID. Now gathered on a single platform, the Raman and infrared information is combined where it undergoes additional analysis, with combined-search results in hand within seconds. The entire process, from independent data collection on each device to advanced search results, is complete in less than 2 minutes. Because the HazMatID can store both the Raman and infrared results, in addition to the combined search results, the data can be sent to ReachBack. Summarizing, although either instrument may independently identify the unknown hazardous sample, the ability to automatically integrate multiple data sources can be vital, and allows the emergency responder to say to their incident commander "I verified the identity of the unknown based upon the following multiple data sources…".

"Ultra" discrimintation using Raman and Infrared

Occasionally, unknown samples produce spectra (IR or Raman) quite similar to other species in the library and result in an identification hit-list with multiple species with nearly equivalent correlation scores. As a simple example consider the HazMatID results displayed in Figure 1 for hexane. Indeed, the identification hit-list reveals very high similarities for the top 5 hits (all above 0.97!), yet with hexane below the top hit list. Based upon the IR results alone a first responder can only determine that the unknown sample is a saturated hydrocarbon at best. Though this still provides valuable information about the potential hazards of the sample, a 20 second analysis on the RespondeR (Figure 1) reveals better discrimination amongst the hit-list in this case – a detail that isn't too surprising since Raman spectroscopy is much more sensitive to subtle differences in the molecular (carbon-carbon) backbone. Faced with results that are slightly dissimilar, the user can utilize the new software and resolve this discrepancy by wirelessly transferring the Raman data with a single button push for further analysis on the HazMatID in seconds as highlighted in Figure 1. Advanced analysis using the two pieces of information results in a hit-list that contains only hexane and with a higher degree of confidence. Though a benign case, since the response protocol is the same for all the species listed, it simply serves as a proof-of-principle example to demonstrate how two different Smiths instruments can be used in combination to provide more accurate answers.

What a difference it can make

In most hazardous incidents the scenario is not as benign as discerning hexane from heptane. For example, consider an apartment raid of a suspected terrorist where an unidentified colorless liquid was found in a closed, unlabeled glass container. Unaware of the container's contents the emergency responder employs both the HazMatID and RespondeR devices in a systematic approach to identify the unknown. To avoid handling the sample directly, the user first utilizes the RespondeR instrument, operating in a point-and-shoot mode, which results in two library matches with reasonably close similarity scores: allyl alcohol and octadecanoic acid (i.e., stearic acid), as displayed in Figure 2. Indeed, verification of the Raman analysis is vital because the first compound, allyl alcohol, is an extremely volatile, toxic industrial chemical with an IDLH of 20 ppm.[3] Octadecanoic acid, on the other hand, is a fatty acid commonly found in animal food products. Extracting a few drops of sample from the container and analyzing it on the diamond sensor of the HazMatID results in a top hit of allyl alcohol (Figure 3), however, with a similarity score below the recommended 0.95 limit (S = 0.8983). Additionally, the next top hit on the IR instrument is identified as D-sorbitol and has a relatively similar correlation value with respect to allyl alcohol. In a predicament, yet with IR and Raman information in hand, the user instantaneously transmits the Raman data to the HazMatID where the software automatically integrates the information and performs advanced analysis within seconds to verify the container contents as allyl alcohol.These results are very valuable in the context of the other materials found in the apartment since the use of TICs in home-made bombs is becoming a greater concern to the Department of Homeland Security.[4] Note, in this scenario the Bluetooth communication is vital because it automatically combines the critical information to allow for advanced analysis to take place instantaneously!

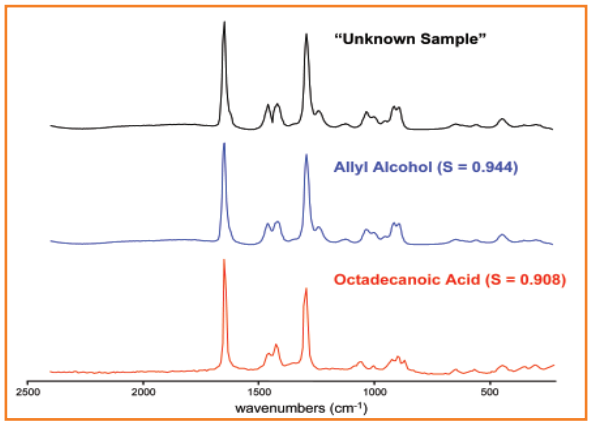

Figure 2. Example of allyl alcohol (blue) and octadecanoic acid (blue), which have very different hazards, yet have relatively similar Raman spectra.

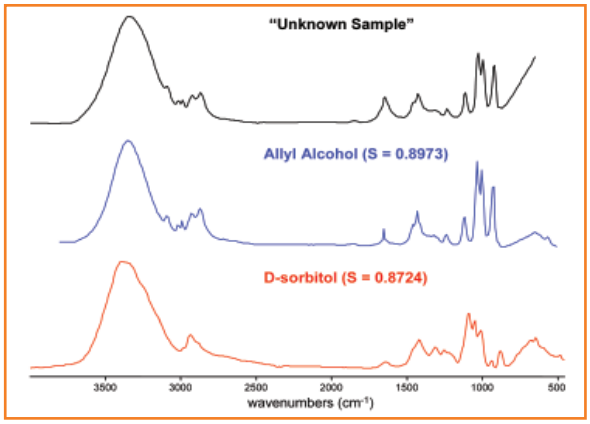

Figure 3. Library match results of an unknown sample showing the similarity scores for allyl alcohol (blue) and D-sorbitol (red).

Summary

In an effort to minimize risk a typical response plan relies on gathering as much accurate and critical information as possible to assess the hazards present during a chemical event. Indeed, manually integrating the various pieces of information can be a time-consuming and difficult process. This application note highlights how Smiths Detection is developing a strategy to ease these difficulties by highlighting how the HazMatID and RespondeR can be used together to identify hazardous chemical unknowns with even greater accuracy.

References

(1) NFPA 472, Standard for Professional Competence of Responders to Hazardous Materials Incidents, 2002.
(2) NIST Handbook 150, Procedures and General Requirements, pg. 51.
(3) www.cdc.gov/niosh/idlh/107186.html (Allyl Alcohol)
(4) www.osha.gov/SLTC/emergencypreparedness/guides/chemical.html

21 Commerce Drive Danbury, CT 06810-8153 Phone: 1 203 207 9700 Fax: 1 203 207 9780 www.smithsdetection.com

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