Application Brief AB-073

RAMAN AND INFRARED FOR HAZMAT RESPONSE

Introduction

Infrared (IR) spectroscopy changed the way First Responders approach chemical events. With a HazMatID in hand, suspicious solids and liquids are identified on scene more quickly and confidently than ever before. Now Smiths Detection offers the RespondeR, a Raman spectrometer that also identifies condensed phase products. This begs an obvious question: "Why do I need a HazMatID and a RespondeR RCI if they both do the same thing?"

Well, the truth is they **don't** do the same thing. While IR and Raman are very similar in their ability to identify covalent molecular substances, each has distinct advantages. IR is most sensitive to dipolar chemical bonds (like alcohols), whereas Raman is better at seeing polarizable chemical bonds (like aromatics). Samples have to physically touch a diamond IR sensor to be measured, but Raman can measure samples inside of vials or plastics bags. Plus, the Raman spectrum goes to lower wavenumbers than the IR, allowing additional classes of compounds (like metal oxides) to be identified. Conversely, Raman measurements sometimes produce fluorescence, a spectral interference that complicates identifications. This application note discusses how the HazMatID and RespondeR RCI are used together such that their respective advantages truly complement each other.

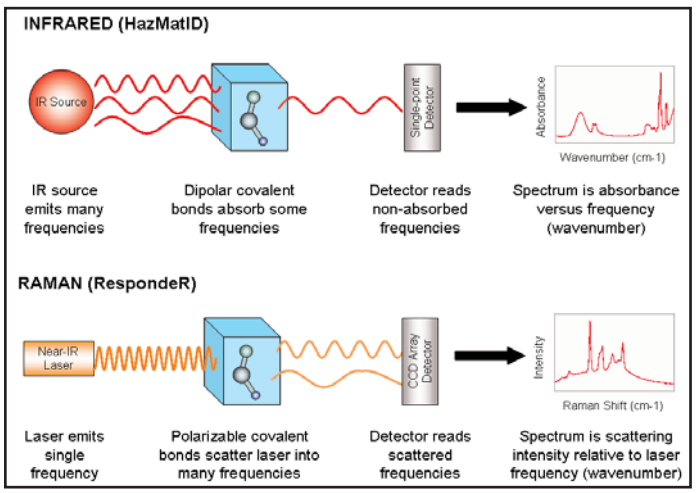
Raman vs. IR Theory

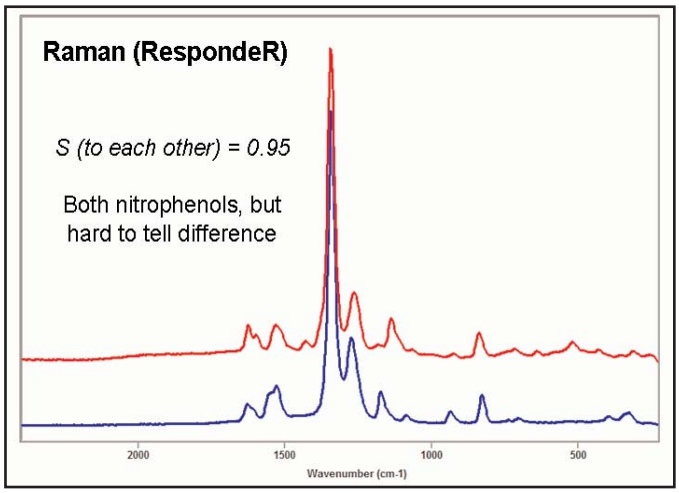
The illustration shows how the HazMatID and RespondeR RCI get different information from the same sample. HazMatID measures how much the various IR frequencies are absorbed by dipolar chemical bonds. RespondeR RCI, on the other hand, measures how much a laser beam is scattered by polarizable chemical bonds. Both techniques produce molecular fingerprints which are used to identify unknown products, and one instrument can theoretically do the job itself. But having both pieces of data gives a more complete molecular picture, providing greater flexibility and confidence when dealing with a wide range of unknowns.

HazMatID

RespondeR RCI

Consider the example of an unidentified yellow crystalline powder found in an unmarked glass vial. Direct Raman analysis of the vial produces two library matches with high similarities: 2,4-Dinitrophenol (DNP) and 2,4,6-Trinitrophenol (TNP, a.k.a. Picric acid). These compounds have similar chemical structures, solid form appearances, and Raman spectra (Figure 1). Correctly, the RespondeR RCI indicates that the unknown is some type of nitrophenol. However, TNP is a highly energetic compound that is listed by OSHA as a Class A explosive[1], while DNP was once used in diet pills and is still used today (though inadvisably) by bodybuilders to quickly shed body fat.[2] The extra NO_2 functional group on TNP clearly impacts the hazard potential of these nitrophenols, and the indirect effect it has on the O-H group (not seen by the Raman) shows up in their IR spectra (Figure 1). Removing a tiny sample from the vial and running an IR analysis could clearly determine whether the solid is a dietary supplement or a contact explosive, which is critical information.





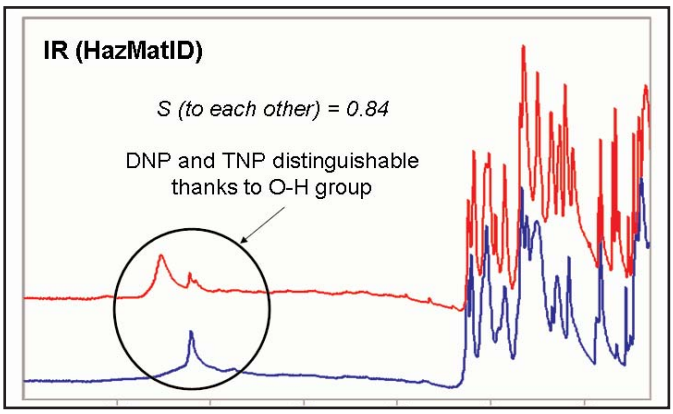


Figure 1. DNP (red, offset for clarity) and TNP (blue), which are chemically similar but have different hazards, can be classified with both techniques and further identified by IR.

Application: White Powders

The above example illustrates that IR and Raman can classify or identify products on their own, but having both techniques available on scene provides invaluable confidence in measurements. Acetylsalicylic acid (a.k.a. Aspirin) is a good example of a drug that produces readily identifiable IR and Raman

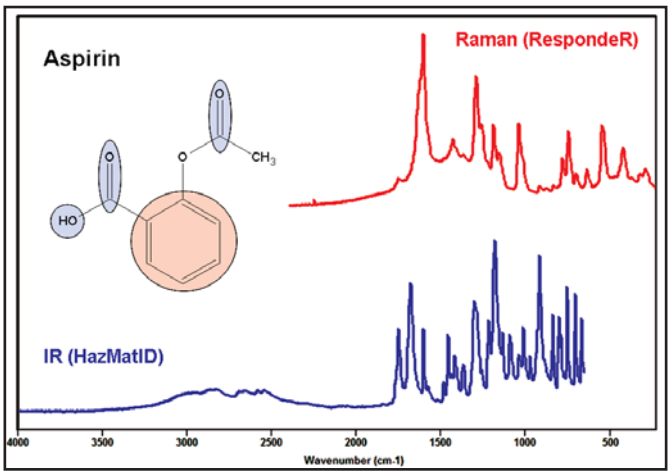


Figure 2. Aspirin is one of the many white powders that produces distinct peaks in both the Raman (red) and IR (blue), thanks to relative sensitivity of each technique to different parts of the molecule (highlighted in red and blue).

spectra (Figure 2). Since different parts of the Aspirin molecule produce characteristic peaks in each spectrum, a combined analysis of these data gives strong evidence that the unknown powder is indeed Apsirin. Having both techniques gives a better chance of seeing impurities or other components, since each is sensitive to different chemical functionalities. As the saying goes, "Two heads are better than one," and the HazMatID / RespondeR RCI combination is a case in point.

Application: Chemical Warfare Agents

While white powders are by far the most common use of the HazMatID and RespondeR for First Responders, TICs and chemical WMD are also concerns. The latter are examples of products that can be problematic for Raman. Chemical WMD typically contain low-level impurities (especially in a clandestine production scenario) which give many of the agent liquids a yellow-brown tint. Raman analysis of these liquids (or most other colored samples) with a 785 nanometer laser (like in the RespondeR and most portable Raman systems) produces fluorescence. This is a spectral interference that shows up as a broad hump in the baseline for agents such as VX (Figure 3).

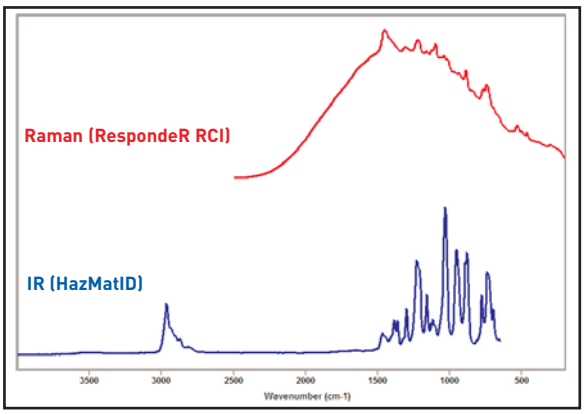


Figure 3. Impure VX, like most colored liquids, produces a fluorescence hump in the Raman baseline (red), but no artifacts in the IR (blue).

Although peaks are still observed in the Raman spectrum which can be analyzed following data manipulation, the final identification is compromised. Nonetheless, an initial screen of a vial containing a yellow-brown liquid with the RespondeR can indicate possible VX. But placing a tiny drop on the HazMatID diamond can confirm VX with greater confidence, since IR is not as sensitive to the same impurities that hinder the Raman analysis.

Application: Corrosive Chemicals and TICs

Acids and bases are a concern for First Responders because of their corrosive and oxidizing properties. Unfortunately, these products are often difficult to identify with IR because they exist as water-based solutions. This is less of a problem for the RespondeR, since Raman is inherently insensitive to the polar water O-H bonds. The Cl-O peaks of hypochlorite are readily observed in a commercial 5% bleach solution with the RespondeR RCI, whereas the HazMatID only sees the water (Figure 4). Using

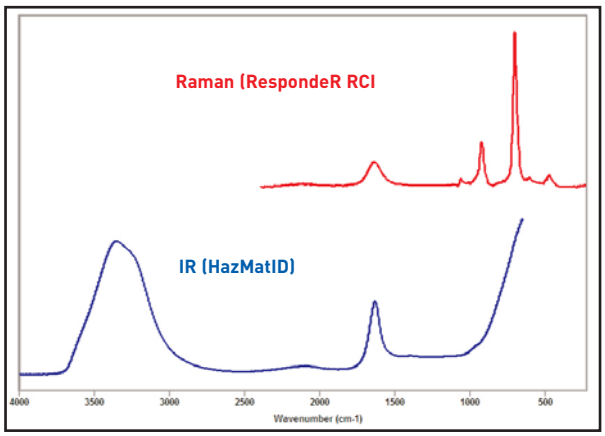


Figure 4. Over-the-counter bleach (5% hypochlorite in water) produces a distinct hypochlorite signature in the Raman (red), but is obscured by all the water in the IR (blue).

both tools together, one immediately knows that the product is a water-based (from the HazMatID) hypochlorite (from the RespondeR RCI) solution, and the situation can be mitigated appropriately.

Summary

Infrared and Raman spectroscopy identify solids and liquids in different ways. The examples presented here show that using the techniques together is the best approach for identifying the greatest number of unknown chemicals accurately and reliably.

References

1. http://www.osha.gov, 29 CFR 1910.109(a)(3)(i)
2. http://en.wikipedia.org/wiki/2,4-Dinitrophenol

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