Advances in Handheld FTIR Chemical Identification for Counter Terrorism and Defence

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1. INTRODUCTION

Vibrational spectroscopy is a mature and well accepted analytical tool used for accurate chemical identification. Specifically, Fourier transform infrared (FTIR) and Raman spectroscopy have widespread acceptance as the techniques of choice for the identification of unknown materials based on their molecular structure[1]. Both techniques are complementary since different molecular vibrations within a molecule have either infrared or Raman activity. However, the selection of a specific method is often based on sensitivity, sampling limitations, and interferences. The primary Raman interferent is fluorescence effects from impurities often found in field samples. Even a small fraction (<1%) of a fluorescent contaminant can significantly occlude a Raman spectrum. Post-processing algorithms designed to compensate for a fluorescent background produce inconsistent results. Water is the primary interferent associated with FTIR spectroscopy. Infrared absorption of water generates broad spectral features that can mask the presence of materials of interest. Water extraction and post-processing algorithmic techniques can be used to reduce the deleterious effects of water interference. Raman spectroscopy has the attractive attribute of being able to analyze samples through bags and bottles while FTIR methods require direct contact with the sample.

Based on these considerations it is not surprising that molecular spectroscopy and FTIR instruments in particular are the chemical identification tools of choice used by emergency responders and military personnel[2,3]. To be useful in those challenging applications, a chemical identifier must be highly specific, accurate, easy to operate while the user is suited in protective gear, rugged, portable, and able to withstand decontamination procedures. Analytical instruments in those challenging applications must have high specificity in order to identify the broad range of threats that may be encountered. Those threats can include toxic industrial chemicals (TICs), explosives and explosive precursors, nerve agents, pollutants, illicit drugs, and suspicious white powders. For instance, NATO's international Task Force (ITF)-25 prioritized 98 potential TICSs considered to be a hazard in a military or civil scenarios. The ITF-25 high-hazard list contains a wide variety of compounds with different physical and chemical properties (organic, inorganic, corrosive, hydrides, flammable, reactive, etc.). From the emergency response perspective, there are approximately 5,000 hazmat incidents per year primarily in fixed facilities (80%) and transportation (20%). In the US, approximately 850,000 businesses use, produce, and/or store a wide variety of toxic chemicals. PoisIndex™ lists 627,000 toxic chemicals in existence worldwide, and roughly 600 new chemicals are created every year. Considering that on average there are 500,000 hazardous chemical being shipped every day (1.5 million tons/year), even a very low probability of an accident still results in a significant number of events requiring a hazmat response. Those statistics[4] validate the increasing demand for portable, selective, and broad range chemical identification instruments.

Other requirements for the use of FTIR instruments in military and emergency response applications are portability and ruggedness. Unlike a conventional laboratory grade instrument, field deployable devices must be transportable and battery operated. In addition, those instruments must meet a wide range of mechanical and environmental specifications pertaining to drop, vibration, temperature, humidity, and altitude. Moreover, the chemical identifier must also be able to withstand decontamination procedures that could range from a wipe-down to a full immersion using a detergent solution. The challenge for instrument designers is to balance these stringent customer requirements against conflicting design parameters affecting the performance of the system.

2. THE HAZMATID ELITE

2.1. Product History

Smiths Detection[5] offers portable and handheld FTIR systems to the military and emergency response community for the identification of unknown solids and liquids (Figure 1). The HazMatID is a man-portable FTIR chemical identifier with a table-top form factor. The instrument was introduced in 2003 and has since been deployed over 3,500 times worldwide. The sampling interface is an easy to use, clean, and maintain diamond attenuated total reflectance (ATR) device. The key to ATR sampling is bringing the unknown material into intimate and uniform contact across the entire surface of the ATR element. The HazMatID can be used in conjunction with Smiths' Raman instrument (RespondeR RCI™) to provide orthogonal or confirmatory capabilities.

A significant software and communications upgrade was realized in 2010 in an effort to further expand the HazMatID performance and capabilities. The HazMatID 360 upgrade[6] included primarily the addition of Functional Group Overlays, the PEAC® database reference[7] to aid in chemical identification for emergency response, a new graphical user interface, and most importantly, the integration of a novel mixture search algorithm. The HazMatID 360 algorithm uses a two-step search approach combining a pre-screening peak table search followed by a detailed explained variance analysis of the screened spectra. This method results in a significant improvement of the search results for mixtures without compromising the performance of pure chemical analysis. Moreover, the search can be completed in about 15-30 seconds depending on the size of the library.

Figure 1. The HazMatID 360 FTIR chemical identification system.

2.2. The Next Generation Handheld FTIR

The HazMatID Elite instrument (Figure 2) is designed to meet or exceed the stringent Military Standard 810G requirements of ruggedness, usability, and performance. This chemical identifier maintains or exceeds the performance of its man-portable HazMatID counterpart using 10% of its volume and 20% of its weight. The handheld HazMatID Elite instrument uses the same HazMatID 360 mixture analysis algorithm to provide high accuracy and low incidence of false alarms for the identification of pure samples and multiple component mixtures. The instrument is capable of identifying chemical warfare agents, explosives, toxic industrial chemicals, narcotics, and suspicious powders. The HazMatID Elite incorporates improved processor speeds and optimized search algorithms to provide unknown search answers in record speeds.

Figure 2. The HazMatID Elite FTIR instrument

The optical engine is designed with a resistively heated wire source, a fiber optics laser diode reference, cube corner reflectors, and a thermo-electrically cooled deuterated L-alanine doped triglycine sulfate (DLaTGS) detector. Cube corner reflectors[8] are mounted on two arms of a double pendulum modulator[9] driven by an electromagnetic actuator. In this configuration, interferogram scans are collected by sweeping the reflectors over the required optical path difference. Because both reflectors move synchronously, each reflector travels half the linear distance required in a traditional Michelson interferometer. This optical engine was selected over the standard Michelson design because of its tilt compensation, reduced motion, inherent self-alignment, and disturbance rejection. As demonstrated by over 60,000 hours of operation and more than 100 drop tests performed in-house, these attributes provide unprecedented stability and robustness against vibration and shock. Significant engineering effort[10] was dedicated to reject vibration interferences, develop protective structures to further ruggedize the instrument, and to improve the thermal loads necessary to achieve an operational temperature range (between -20 °C and +50 °C) that is unmet by any other existing chemical identifier.

The HazMatID Elite instrument incorporates long-range (1 Km line of sight) embedded RF wireless transmission for rapid data communication out of the hotzone to aid in information integration, decision making, and connection to ReachBackID™ support services. The system also includes a GPS that allows tagging the coordinates of the location of the sample to the results file and FIPS 140-2 compliant encryption. Advanced spectral analysis using extended databases, automated communications to Smiths Detection ReachBackID services, and remote monitoring of the FTIR instrument can be achieved wirelessly with a separate command system. The HazMatID Elite sampling options and user interface have not been introduced previously and will be discussed in separate sections.

2.3. User Interface

The HazMatID Elite instrument includes a state-of-the-art intuitive user interface. The 4.3 inch liquid crystal display (LCD) has a large viewing angle and is coated with an antiglare thin film for readability in direct sunlight conditions. The large keypad controls are designed for intuitive operation and tactile properties for effective use in protective gear. The keypad also incorporates smart keys that are lit only when, for each specific screen, the function of a key is active. Persistent status icons and configurable audible and visual alarms are used to elevate the communication of critical information to the user. On-screen instructional graphics guide the users through the essential operations of the device, to maximize ease-of-use, and reduce the training burden. For instance, the use of color-coded menu options, simplified workflows, and graphical instructions improve the customer experience and simplify the access to common activities (start-of scan results in just 3-clicks of a single button). The user can configure up to 100 alerts for prioritized rapid identification of CWAs, explosives, narcotics, and TICs (Figure 3, left).

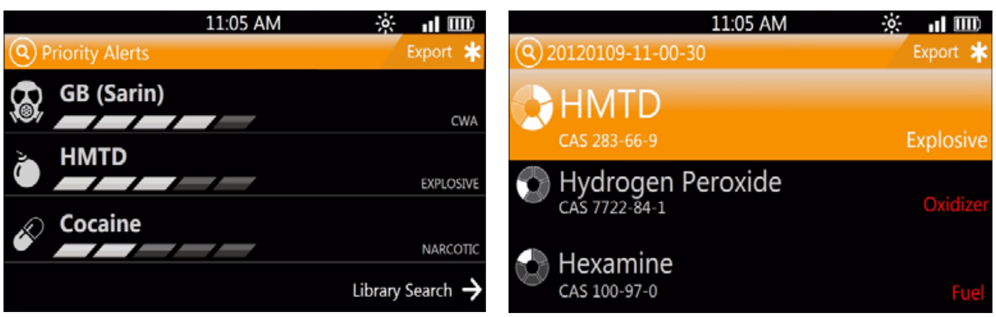

Figure 3. Priority alert and library search result screens.

With a single push of a button, the results can be exported to incident command for rapid incorporation into the strategic action plan. The library spectrum includes 10,000 chemicals tagged with class and hazard information and is compatible with HazMatID user libraries. Based on the proven HazMatID 360 search algorithms[6], the next generation handheld instrument provides accurate multi-component unknown mixture identification displaying the relative contributions approximated in pie chart format (Figure 3, right).

2.4 Sampling Alternatives

Portable FTIR instruments used for condensed-phase chemical identification in military and emergency response applications commonly use an Attenuated Total Reflection (ATR) sampling interface. The method involves pressing a small amount of unknown substance onto a small diamond ATR surface. This technique provides fast and simple operation even when the user is suited in restrictive protective gear. The HazMatID Elite's dual ATR option and available sampling tool provide three options to address different sampling challenges.

2.4.1. Integrated Press

The key to successful ATR sampling is that the unknown material be brought into intimate and uniform contact across the entire surface of the ATR element. The most consistent method to achieve contact uniformity with solid samples is to place the material on top of the ATR element and to apply a constant pressure. The HazMatID Elite instrument incorporates the proven and robust solid press design pioneered with its table top counterpart (Figure 4). The procedure for using the press is for the user to place a small (grain size) gathered sample on the ATR element and with one hand, push down the lever that presses the material onto the optical element. This reliable and reproducible integrated device overcomes the contact inconsistencies associated with the competitive approach of using a detachable, spring loaded press assembly. Using this detachable accessory involves the additional steps of placing the sample on the accessory and carefully clamping the device to the touch-to-sample tip. Decontamination challenges and possible loss of the accessory have been reported as limitations of the approach. The HazMatID Elite solid press is also designed with a liquid well for sample containment and open flat surfaces for easy sample introduction and cleaning.

Figure 4. HazMatID Elite integrated press with liquid well

2.4.2. ClearSampler Surface Sampling Accessory

The Clear Sampler (Figure 5) consists of a single-use swab disk and a ruggedized handle optimized for use in protective gear. The accessory utilizes a micro-mesh structure, developed by Orono Spectral Solutions Inc., Bangor, ME, to allow collection of unknown substances presented on thin films and contaminants scattered on surfaces. Sample swabbing with the ClearSampler takes only a few seconds and the mesh disk element can be placed directly on the ATR sample interface without the need of any additional sample preparation. Unlike other swab materials such as cotton tip applicators, the active surface of the ClearSampler is not infrared active and therefore does not produce an interferent signal that competes with the target chemical. The swab disk can be archived for future analysis using other analytical techniques. As discussed in the following section, the ClearSampler expands FTIR applications in decontamination verification, explosives residue analysis, and hazardous material interrogation.

Figure 5. ClearSampler accessory

2.4.3. Touch To Sample Sensor

The HazMatID Elite can be configured with a second touch-to-sample (TTS) sensor to easily identify spilled liquids without the need for time consuming and equipment intensive liquid sampling (Figure 6). Transition between press and direct sampling is simple and does not require hardware modification or accessory attachments. Data collection is automatically started once sufficient infrared signal is measured thus limiting operator workload and manual intervention. The TTS sensor is designed for use in the hot zone while responders are wearing full personal protective equipment (PPE). The TTS ATR interface is highly effective for direct interrogation of surface contaminants, robotics integration, and quick presumptive analysis.

Figure 6. Interrogation of liquid on cardboard box using the integrated Touch-To-Sample (TTS) sensor.

3. EXPLOSIVES FIELD TESTING

The United States Bureau of Alcohol, Tobacco, and Firearms lists nearly 250 different explosives materials[11]. The identification of these explosives and their residues has become an important military and emergency response mission. The rise of homeland and international incidents involving the use of home-made and improvised explosives requires the use of portable analytical instruments to quickly and accurately determine the composition of these explosives in presumptive and forensic investigations. The nature of such events makes the collection of samples and analysis challenging. After a blast, the explosive residues get scattered in the crime scene onto surfaces and areas difficult to access and to collect evidence. These explosives residues are often mixed with dirt, organic, and inorganic substances further complicating spectral identification of the unknown materials. The HazMatID Elite combined with the ClearSampler accessory provide the optimal sample collection and mixture analysis solutions to address challenges associated with explosives field analyses. It is important to note however, that the HazMatID Elite is not considered a trace detector so positive identification requires the presence of visible quantities of solid or liquid substances. Recent reviews of instrumentation designed to detect, identify, and quantify bulk[12] and trace[13] quantities of explosives are available and will not be discussed in this paper.

The HazMatID Elite capability to identify explosives in real field scenarios was evaluated and tested at NEK (Lake George, CO, USA) and Cranfield University (Shrivenham, UK). As expected, the instrument successfully identified all the tested explosives (RDX, PETN, ANFO, TATP, HMTD, EGDN, ETN, NG, UN, and TNT) in pure form and as a residue (50 μg) from solution. One field experiment involved detonating a small charge (less than 10 lbs) comprised of ANFO and RDX placed in the passenger side door panel of a vehicle. The explosive charge did not detonate entirely as intended, but rather went low order and disseminated ANFO and RDX inside and around the vehicle. The charge tore the door panel apart and shattered the windows, but otherwise caused little damage. The ClearSampler tool was used to swab residue from various surface areas and locations. In some instances the sample residue was present as a fine dust that would be nearly impossible to collect using traditional methods. Material collected from the steering wheel of the vehicle (Figure 7, left) was collected using the ClearSampler and analyzed using the HazMatID Elite identifying ammonium nitrate as the primary component. Post-blast residue collected on the roof of the driver side of the vehicle was also interrogated showing spectral features consistent with RDX (Figure 7, right). In all these instances, the use of the ClearSampler was instrumental in facilitating and simplifying the evidence collection process.

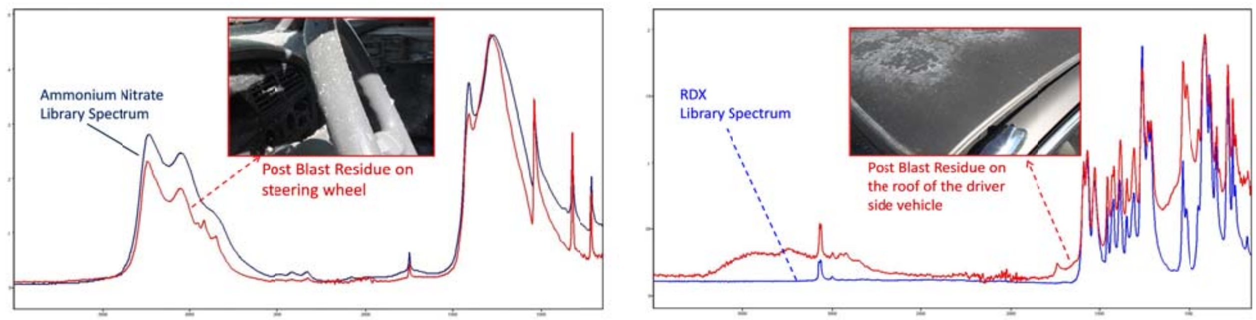

Figure 7. Analysis of explosion residue collected inside and outside of vehicle.

4. CONCLUSION

There is an increasing need to miniaturize equipment and simplify the use of analytical tools used by soldiers and emergency responders in the field. The HazMatID Elite chemical identifier is the result of a careful balance between size, weight, power specifications, ruggedization, spectral performance, and sampling flexibility. The new hand-held FTIR product incorporates advanced algorithms and a simplified user interface to provide concise and actionable information in record time. The ClearSampler swab accessory, designed to work optimally with the HazMatID Elite, simplifies the collection of unknown substances. The HazMatID Elite capability to identify unknown substances in mixtures combined with the ClearSampler ease of use to collect sub-microgram quantities of scattered samples is the ideal solution to address the challenges associated with explosives field analyses.

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