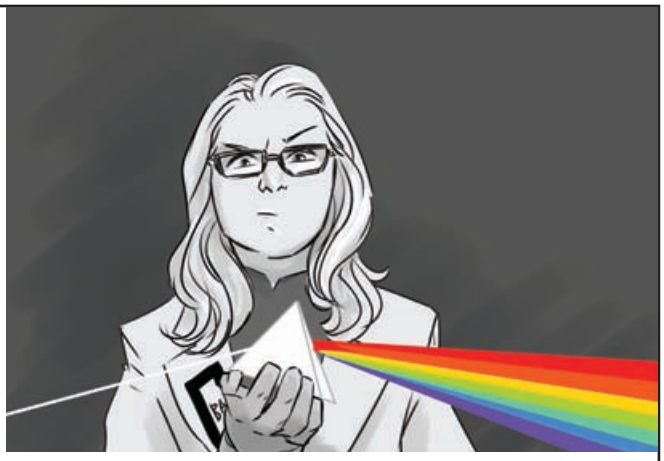
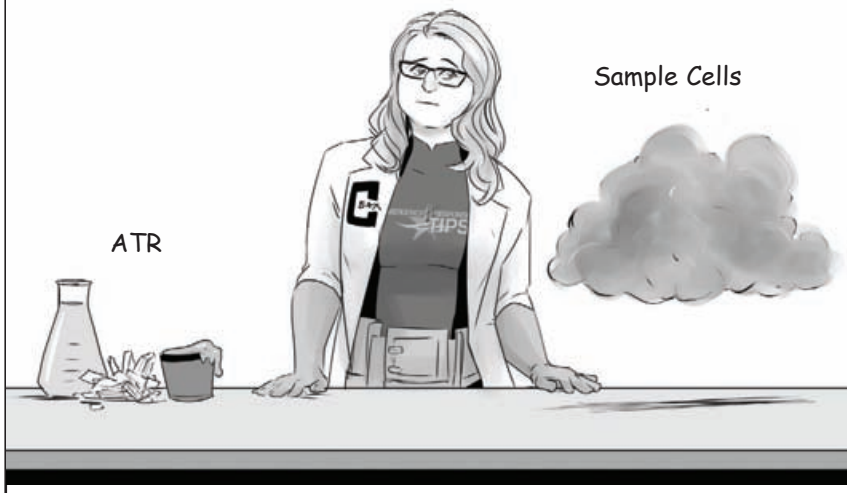
Dr Christina Baxter, of EmergencyResponseTIPS.com and Hazard3.com, offers helpful advice for first responders

Keeping you safe!



This column aims to provide operational guidance to the hazmat/CBRNE community on the selection and performance of equipment and tactics. In this issue we are focussing on the purchasing considerations and applications for Fourier Transform Infrared Spectroscopy (FTIR). While the physics behind infrared spectroscopy was demonstrated in the early 1900s by Coblenz, it was 50 years later that the mathematics behind FTIR spectroscopy were introduced and over a further decade until the fast FTIR concept we commonly use today appeared in 1965.

Instruments were mostly laboratory based; it took another 35 years before the first field-ready FTIRs using attenuated total reflectance (ATR) for analysis of solids and liquids were launched by SensIR Technology in 2002 (TravelIR) and 2003 (HazMatID). Today, there are several products on the market suitable for field operations, ranging in applicability across all states of matter, sample collection and preparation requirements. They also incorporate spectral libraries and easy to use software applications.



Making a choice

Most commercially available, field ready instruments are either for solid/liquid or for gas applications, although some instruments provide both, using swappable interfaces. It is important to identify the states of matter and sample types of interest prior to selecting the FTIR.

When identifying and selecting an instrument, the user should set their selection criteria, by considering the performance requirements such as instrument resolution, measurement range, detector, measurement approach (eg ATR, crystal type) and operating conditions. Further important considerations include instrument construction, robustness, power, weight, screen, EMF protection, ability to decontaminate and ease of operations.

Liquid/solid sample preparation

For solids and liquids, a sample must be taken and transferred to the FTIR sample interface. Most field deployable instruments use ATR. A background (crystal only) is first collected followed by the sample spectrum. In this case, the IR beam is reflected off the underside of the crystal and some of it leaks into the sample. The infrared spectrum is created by subtracting the background from the sample spectrum. ATR-FTIR spectroscopy allows for the collection of high quality, reproducible

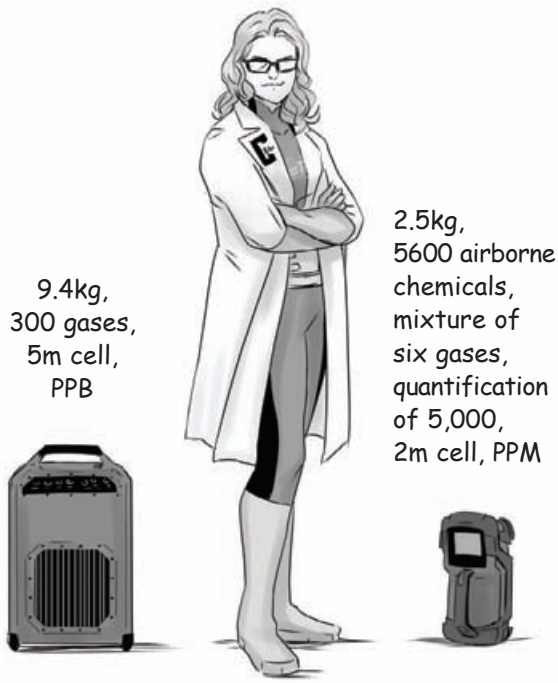
FTIR spectra with minimal sample preparation.
Samples must have consistent contact with the ATR-FTIR sampling surface. Liquids naturally create consistent contact on the crystal, but solids often do not, and so they need to be pressed to improve contact using an anvil. Care must be taken to ensure that shock sensitive materials are not placed under the anvil. Many systems provide a ring to focus the liquid droplets onto the crystal, but it is not always necessary.

Gathering a representative sample is the most important and time-consuming part of the process for liquid and solid samples, and is a step which is inherent to all sampling strategies, not just those associated with ATR-FTIR. It is recommended that at least three samples are taken from the material under investigation, alternatively the sample can be mixed or ground to improve homogeneity.

The most used ATR-FTIR spectrometers in the hazmat/CBRN field today include the 908 Devices ThreatID, 908 Devices ProtectIR, Smiths Detection Hazmat ID Elite, Thermo Scientific TruDefender FTX, and the Thermo Scientific Gemini.

Gas sample collection
For gas phase samples, a traditional detector (ie flame spectrophotometer or photoionisation detector) is often used to find the source of the unknown gas and then a sample can be analysed by gas phase FTIR. But note, some gases, like chlorine, cannot be analysed by FTIR. This market is currently dominated by two products - the 908 Devices (formerly RedWave Technology) XplorIR and the Gasmet T5000 Terra - each targeting a different operation. There are also teams using traditional laboratory-based gas phase FTIR instruments in field operations.

The XplorIR is a handheld system weighing 2.5kg (5.5lbs). It can simultaneously analyse more than 5600 airborne chemicals, providing both a mixtures analysis of up to six gases and quantification for up to 5000 gases, at parts per million (ppm) levels with detection in seconds and quantification in under a minute. XPlorIR provides an adaptive atmospheric correction process to minimise the effects of humidity and carbon dioxide on spectra. Remember, a sample taken at 21°C (70°F) and 80% humidity will have approximately 1400ppm water vapour present and 500ppm carbon dioxide present in addition to the chemical of interest. These levels would overwhelm the hazardous materials present and therefore must be dynamically removed if chemical identification is desired at the ppm level.



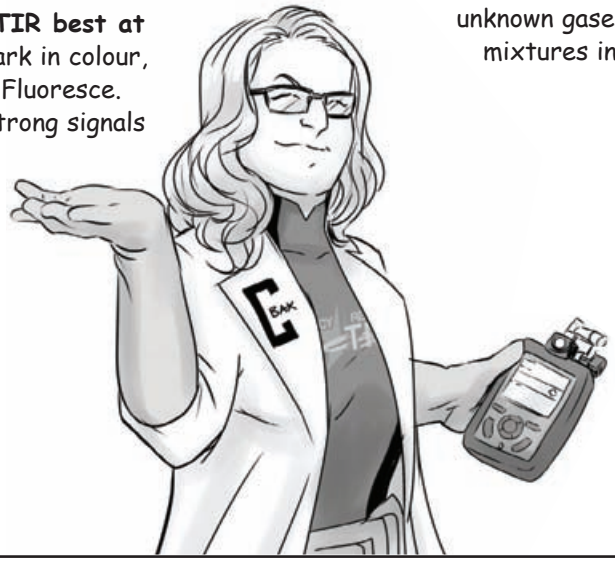
The Gasmet T5000 Terra is a backpack system (9.4kg) capable of simultaneously analysing up to 50 compounds chosen from a library of over 300 gases in less than two minutes. This device can also identify and quantify the chemicals of interest at low ppm levels. The T5000 Terra uses a five metre sample cell to achieve low detection limits while the XplorIR uses a two metre cell. The difference in cell path lengths becomes important when lower levels of detection are required. Generally, two metre cells measure materials in ppm while 10 metre cells measure in ppbn, therefore, the T5000 Terra can likely reach lower levels of chemicals of interest.

Keeping you safe!

Library
An FTIR spectrometer without a library is not suitable for field operations. Standard spectral libraries are available for FTIR spectra for gas, liquid and solid phases. Library sizes vary but are generally in the greater than 20,000 compounds range. It is important not to confuse ATR-FTIR spectra with Transmission-FTIR spectra as there are small variations in peak positions and intensities, which can result in inaccurate identification.

Software
Current library matching algorithms tend to incorporate a combination of hit-quality index and chemometrics approaches to identify and name the sample chemical. The differentiator between commercial products generally is in the mixture algorithms. It is a known limitation of solid/liquid ATR-FTIR that systems tend to only identify those components of a mixture that exceed 10% of the total sample matrix. As advanced algorithms and chemometrics techniques are applied, however, the mixture analysis can be more accurate at the lower levels. Similar approaches are used to identify and quantitate components within gases.

Applications
FTIR spectroscopy is used in field operations to identify unknown substances. It is a complementary technique to Raman spectroscopy, discussed in the December 2019 issue. FTIR spectroscopy of solids and liquids is suitable for materials that are dark in colour, fluoresce and have strong signals but doesn't perform as well with samples diluted in water. Raman spectra tend to provide excellent spectral quality on non-polar bonds while FTIR spectra provide excellent data on the polar functional groups, making these techniques truly complementary. Gas phase FTIR technology allows for near real time detection and identification of unknown gases and gas mixtures in the field.



Stay safe out there!

CBax away!

Images are courtesy of Phil Buckenham *https://philbuckenhamart.wixsite.com/philbuckenham*