On the vapour trail

Just because there is no vapour detected doesn't mean that it is not chemical ©CBRNeWorld

Dan Kaszeta looks at the options available when identifying low-volatility chemical hazards

The identification of low-volatility chemical hazards can pose problems for the first responder. Much of the research effort and expenditure in the chemical detection market has focussed on the military chemical warfare agent (CWA) threat. Chemical warfare agents are wide-area lethality or injury hazards because they pose a respiratory threat. In order to pose a respiratory threat, chemical warfare agents and toxic industrial chemicals generally need to have a vapour pressure and some volatility. Even the most persistent of the CWAs, HD and VX, have some vapour pressure in normal field conditions. But the reality is that not every threat, military or civil, is going to be measureable on an instrument designed to detect gas and vapour. Rather a lot of hazardous substances have low volatility and low vapour pressure. Numerous commercial and industrial chemicals of interest exist primarily in liquid form, with a negligible presence of vapour in normal conditions. In addition, cold temperatures may create situations where substances that might have some vapour pressure in warm weather have little or none at cold temperatures.

Having been actively involved in *CBRNe World*'s Directory project I've cast my eyes over practically every piece of chemical identification equipment currently marketed to responders. During the process it occurred to me that there are only limited options available to help identify low-volatility chemicals. The simplest way of stating the identification problem is that, in an accident or incident, a responder needs to get information from the low-volatility chemical. Having a gas or vapour coming off the chemical provides a number of ways to get information from the substance. When the problem is in liquid or solid form only, the responder is effectively robbed of several useful analytical techniques. The options available in these circumstances are to get into close contact with the substance, interrogate the substance from a distance, or try to turn the liquid into a gas or vapour. I'll deal with these in reverse order.

Many of the analytical techniques available to the responder are geared around gas and vapour threats. It is not an approved technique to shove a powder into a Dräger tube or suck a liquid into a PID. Actually, you can do it, it's good for a laugh at the bar afterward, but its not a useful analytical technique (I once chased a responder down the hall with a broom handle for wrecking a PID this way). Many situations may be on the borderline, i.e., there may be some vapour, just not enough with which to do anything useful. Placing a bit of the liquid in a plastic bag or under a bucket for a few minutes (the latter being the old VX trick from the US Army's toxic agent training at the CDTF) might increase the vapour enough. Also, some analytical techniques involve collecting a sample in a thermal desorption tube, so a responder could theoretically let the sample pump run for ten or 20 minutes, thus concentrating what little vapour may be there. Vapour pressure exists in relation to temperature, so putting a sample in the sun or finding a way to warm it might induce more vapour.

Some techniques allow for interrogation from afar. In other words, there may be ways to get the liquid or solid sample to give up some information without needing to handle the substance. In practice, this means using a laser, and the 'afar' actually means 'really close, but not actually touching'. The practical devices generally available on the market for this task are Raman laser devices. These devices work by shining a laser into the suspect substance at close range (cm) and observing what light is scattered back from the substance. Many compounds display the 'Raman scattering effect' and have a predictable Raman spectrum that serves as a relatively unique fingerprint. T he operative word here is 'many' however, because not every compound of interest will display the Raman effect. Complex mixtures of products will result in overlapping Raman spectra, which will vex most instruments. Like many technologies, the ability to identify will be constrained to the identifier's library. Finally, a laser-based system will, by definition, impart energy into the substance being identified. Although Raman lasers are low-energy, there is a degree of hazard here, when potentially energetic or flammable materials are involved. The danger is generally with powders than with liquids, as liquids will diffuse the heat, while a single grain of powder may receive most of the laser's energy. In a nutshell, Raman is useful, but will not work in every situation.

Other standoff techniques theoretically exist, most of which involve lasers, but few have made it into field use. Whilst most of the laser work has been done in vapor/gas detection, active neutron interrogation is theoretically feasible and is used in some high-end, EOD applications. Bombarding an unknown chemical with neutrons to see what happens at its sub-atomic level does get some interesting information. The equipment is heavy and expensive however, and requires a lot of training, safety precautions and regulatory paperwork. It may be difficult to discriminate between various complex hydrocarbons, , where the difference in one atom in a molecule may make all the difference between a toxic compound and an inert one. Active neutron interrogation is a sledgehammer that won't always kill the fly.

The most useful options for a responder involve actually handling the unidentified substance. Once a responder has a physical sample collected, the menu of available techniques multiplies. The techniques most useful here (which are also progressively more expensive) are wet chemistry, Fourier Transform Infrared (FTIR), and gas chromatography/mass spectrometry (GC/MS). Wet chemistry techniques in field use typically rely on some visible colour change that the responder can see. Such techniques can vary from quick and cheap (pH paper and Spilfyter strips for example) to complicated chemistry sets, such as the venerable HAZCAT kit. You get what you pay for with these, i.e., the less expensive wet chemistry techniques will, at best, give you a classification rather than a definitive identification.

FTIR is a powerful tool here. Devices such as the Smiths HAZMATID and the Thermo (ex-Ahura) Tru Defender are some examples. There are large libraries with many thousands of FTIR spectra, and far more substances are available than for Raman devices. The key word here is large, not infinite. Not everything has an IR absorption spectrum that can be analysed by an FTIR device. Some substances are also very close to each other. Mixtures can still present a challenge, although both operational techniques and software algorithms give more capability than in previous years. Because the available FTIR devices require a sample of the material, cross-contamination potential requires vigilance, lest you identify a bit of yesterday's sample stuck to the interface (Don't laugh... I've seen it done).

GC/MS remains the gold standard in this area. Twenty years ago a GC/MS device was big, very expensive and lived in a laboratory. Today, with help from companies such as Bruker, FLIR, Smiths and Inficon, GC/MS devices are not so big (still, not very small), a bit less expensive (but not at all cheap) and usable by a field-technician. GC/MS devices are powerful tools that will bludgeon an answer out of all but the most stubborn substances, but they are certainly on the high end of the chart of field technologies. They do not work as quickly as many other techniques (but they are faster than running through a full HAZCAT routine), so a queue will build up if there are a lot of samples for analysis. Certainly, efforts to make GC/MS more compact, cheaper and easier to use and maintain will give more responders the option of using this highly-effective technique.

The real answer to the problem is no surprise to veteran responders. The skilled technician will combine techniques and technologies to find answers. I always thought that combining Raman and FTIR in a single device would be a 'killer app', but that's just my own opinion. Llet's not forget that a few basic principles: getting no response on an instrument is actually very useful for ruling things out, the fact that a substance displays no Raman effect or has a flat line FTIR absorption spectrum rules out an awful lot of things. We must also avoid being narrow-minded and focussing exclusively on the technical means of identification. I once supervised an exercise where several responders flailed about for an hour trying to identify an unknown liquid leaking from a drum in the back of a truck. Lots of clever things were done with meters. A sample was even collected to go to a lab. Reachback was called. But nobody rolled the drum over to see the markings. Nobody talked to the driver, who was being transported from the scene in an ambulance but was still conscious, and nobody checked the cab of the truck for the shipping papers, which were still there. HRW

PID and IMS may not be enough for some samples ©CBRNeWorld