Gwyn Winfield looks at improvements in narcotics detection

Drugged up

When it comes to chemical identification arguably no field is harder than narcotics. The ideal in hazardous chemical manufacture, whether for the battlefield or the industrial space, is to have as good a product as possible. Arguably there is a financial cost to that, but it seems unlikely that in any point of manufacture did the conversation between the chemists go: 'I think I might dump some of this in to bulk it out.' 'What will that do to it?' 'No idea, let's see!'

All the agent fate issues that bedevil CWA detection are there. While you might not be fishing for samples in the bottom of a shell crater, you might be doing something similar in the remains of a suburban house. CWA and TICs are created to set recipes that might vary in strength and precursors, but will retain the underlying signal/spectra. The modern drug market is plagued with 'experimental chemicals' that pertain not to be for human consumption and change every month or so. Yesterday's Hulk Dust is tomorrow's Flakka; and while some of the spikes and signals may be comparable when you are unsure of the toxicity of a substance that can make a significant difference to response.

Volume can also vary, from many kilos of near pure toxic pharmaceutical to tiny elements hidden in tablets that are mainly composed of kitchen cupboard junk, yet can still deliver an effective, if not lethal dose. For the individuals doing the detection, identification and monitoring the hazard is not just a matter of the chemicals themselves, but also the surrounding environment. People who make or sell drugs tend to vary between the aggressively private through to the sociopathic paranoid and as such have a tendency to scatter booby

Not only is it the drug lab that is messy, but the product itself - both challenges for the trace detector ©DoD

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traps through their facilities. Deciding to take a lid of a vessel or pick it up could end in an explosive reaction that has nothing to do with the chemical inside.

For many, then, the complexity of the sector has provided the 'day job' that many chemical meters have been missing. The early days of narcotics detection was dominated by wet chemistry but in the past five to 10 years technology has risen to the task and now there is a wealth of different sensors[1]. These stretch from devices that have been created specifically for the job, such as ThermoFisher's TruNarc[2], through to add on modules for general chemical detectors[3]. Thermo launched the Raman spectroscopy based TruNarc in 2012, and since then there has been a general rush to get a Raman device into the field that can do the ABC of MDMA, aka ecstasy.

Cobalt (now Agilent) launched its Resolve in March 2016, and at first glance it might seem like yet another Raman detector muscling for market share. Yet Resolve managed to have its own ace in the hole that no other Raman detector achieved, which was spatially offset Raman spectroscopy[4] (SORS). Raman was popular because it could look through clear transparent material (such as glass or plastic) to the object inside it. This was a massive step up from needing to take the top off a flask, potentially generating an exothermic reaction or something even less pleasant. Yet it was limited by its ability to penetrate some coloured substances and if the container was opaque, like an envelope or a plastic barrel, you were fishing through the toolbox for something else. Something like SORS.

Dr Robert Stokes, head of detection and security business at Agilent has been with Resolve since it began, and explained what the advantages to the user have been. "The obvious one for narcotics, though it is almost universal, is the safety angle. The popularity of fentanyl and its analogues has raised awareness of potential hazards, but people with experience in the field have been dealing with new psychoactive substances (NPS – good presentation on them[5]), materials which are

Chemimage are proposing hyperspectral for a variety of crime scenes and other missions ©Chemimage

extremely hazardous, particularly in the psychoactive affects they produce in small doses. Before fentanyl became popular the sector was focused on NPS, particularly in the UK. The hazard related to these materials can vary depending on the type of material and the concentration. So if you suspect someone is trying to make product in an illicit lab, using a container that has higher strength material from which they make street level doses, there is acute awareness of the hazard. Also you might not be expecting to find fentanyl in some scenarios, and there are many examples where people make a raid without any intelligence that leads them to believe that there might be hazardous materials. Having Resolve means they can examine substances without compromising the evidence or package. This evidential preservation has been another advantage, but primarily it is about safety."

Traditionally one of the problems with Raman detection has been mixes, where one substance is mixed with another that might provide a stronger Raman signal than the target. This is obviously going to be a problem for drugs that have been cut in preparation for sale, especially with fentanyl or carfentanil where an effective dose might be measured in low micrograms. Over time this problem has been eroded by better and better libraries, and manufacturers investing in regular updates as new substances come on the market. Even so, there are some even more specific problems. Fentanyl and its analogues are known as synthetic opioids, whereas heroin or opium are naturally occurring opioids. This means that without a sensitive enough detector you might think you are only seeing heroin, whereas you are dealing with a far more toxic fentanyl analogue.

It is important not to get it wrong. Dr Stokes stated that in library development it wasn't so much the peaks that you look for, but the grass on the side. As he explained: "There are lots of variants of fentanyl on the market and they greatly vary. One advantage of Resolve is that we have an optical system that gives us a good signal to noise ratio, and that in turn allows us to pick out signal from background meaning our algorithm can work on better quality data. One of the traditional problems with detecting fentanyl is that the stronger part of the signal looks like other narcotics, because of the phenyl ring. It is not the big peak in the middle that you need to look at to detect fentanyl, which

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resembles lots of different things, it is the grass on the sides, which is where the ID data element is. Using a good signal on our spectrograph means that in the grass, where you have sugary peaks, you can pick out the bit that helps you do the ID. For example we have been able to ID street level fentanyl through the little wax wraps it comes in and find the fentanyl in the mixture and capture it as a result."

As you might imagine Agilent is very keen on Raman for field identification (the company has a lot of different lab based systems) and see the future being very much more of the same. "There are always improvements in this field but until our proprietary SORS technique was introduced in 2016 the fundamentals of handheld Raman hadn't changed that much. The form fit has changed a bit, extra features, like software, have been added, but little else has really changed. You can fire powerful lasers and do other tricks to enhance the signal but SORS is a very simple and elegant solution- it produces a clean spectrum of the contents of a container in a short timeframe without any additional input from the user," said Dr Stokes. Raman is great when you have an obvious target. The individual can see the flasks, for example, and then walk over to them and grab a spectrum. Yet if instead of a model clandestine lab we go instead to the same lab after either an explosion or a re-creation of the Gunfight at the OK Corral, then it becomes far harder to work out what belongs to where. Raman would still be used, but the whole processing of the scene, especially if someone has been murdered in the exchange would be much longer. Hyperspectral imaging offers the ability to look at a large area, categorise the scene relatively quickly, and not only pull out exotic target substances, such as heroin, but also conventional ones, such as gunshot residue, blood, or other bodily fluids [Ewww! Ed.].

Hyperspectral imaging has been around for a few years, especially in the forensic space, but the devices used to be large, slow, very expensive, and the volumes of data were difficult to digest. Now all those problems have either been solved or minimised, and devices optimised for work in a chemical crime scene. Hyperspectral devices function by looking at how light interacts with an object, be it a spilled bag of cocaine or a cup of coffee, and then builds a hyperspectral data cube that is referenced with the library to see exactly what tinkers with light in that way.

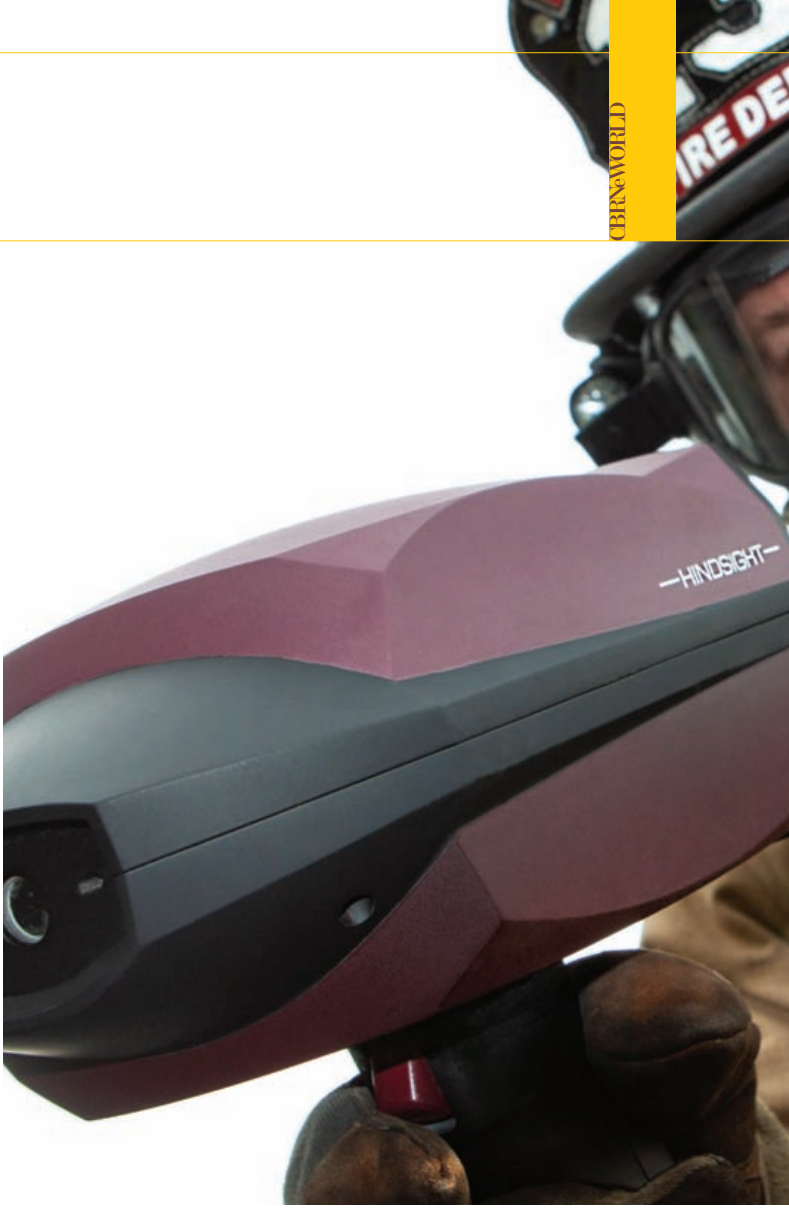
The opportunity now is to be able to scan the crime scene for blood, for example, then flick a switch and scan it for… well, whatever drug is in the library. Due to the prevalence of Raman detectors in narcotic detection there are some detailed libraries ready and waiting to be used by newcomers to the field. While each brand of Raman does its best work with its own library, rather than an imported one, you can get most of the way there without needing to pay small fortunes to government labs to develop your own spectra for super toxic substances. Hyperspectral really needs its own data to be able to scan a crime scene as described above, and this is not cheap. One of the companies making this effort is ChemImage, with its VeroVision all but ready for launch, but is already working on its next generation product, which will utilise a new short-wave infrared (SWIR) hyperspectral imaging technology called the reconfigurable conformal imaging sensor[6].

For those of you, like me, who really have no idea what a reconfigurable conformal imaging sensor is, ChemImage's chief scientist, Matt Nelson, is on hand to explain its advantages and disadvantages. "The conformal filter is a new advancement we have been working on in the past couple of years. The biggest advantage it offers is the means to operate real time, and by real time I mean the ability to detect greater than 10 detection frames per second. It also has a major advantage compared to competing technology like snapshot filters, as the conformal filter is reconfigurable. As new threats become apparent we are able to change the way the sensor works to look at them.

"Regarding the economics, the conformal imaging sensor uses two conformal filters, rather than a single sequential scan filter, as we use with VeroVision. One might think that the cost is double, but actually conformal filters are less complex, so two similar, less-expensive filters mean the final the cost is about the same. The traditional sequential scanning filter has been available for a while, and we understand what it can and can't do to a large degree. What we don't understand yet [with conformal] is its limitation for multi-target sending. To date we have been able to detect up to 7 targets simultaneously, but we haven't yet established the upper limit. We will do so through more testing in the near future. Conformal filtering, like any supervised classification sensor, requires a one-time training step, to get target materials of interest in front of the sensor and background that you might confront in the different operational spaces we work. We are currently trying to establish how many types of targets can we discriminate simultaneously in the presence of these backgrounds. Until we understand that we are not sure what the confines to conformal filtering might be, we are still trying to work out limitations and capabilities."

The reconfigurable conformal imaging sensor is still at prototype stage. Consequently, it is difficult for Dr Nelson to be sure of how complex the scene can be. For example ChemImage provides VeroVision technology in a mail scanner, which allows a stable background, allowing for a large quantity of target analytes to be sequentially scanned. Under circumstances like that hyperspectral imaging will work well. Indeed conformal imaging might work well in highly cluttered scenes, it's just a bit soon to say. "Conformal imaging is not going to be the silver bullet, it won't work for everything, but it will be a useful tool that will get us into real world applications like complex crowd monitoring scenarios, in which the sensor and/or target are moving. That way you don't require the scenario that has both fixed sensors and fixed targets, which makes it a lot more appealing for the application space."

The good news for hyperspectral adopters is that you don't need a separate device to do forensic traces rather than chemicals/narcotics. The change between them is pretty much a



Agilent's Resolve and Hindsight's SpecVur both take different approaches to trace narcotic detection ©Agilent & Hindsight

menu option, meaning that the devices have a great deal of utility. Once the crime scene is in view you can deal with a significant area, the VeroVision can scan roughly a 20 degree horizontal field-of-view. There are attendant factors to these figures however, which are determined by the type and quantity of material and the surface it rests on. The underlying technology used in VeroVision has been demonstrated to detect large amounts of some chemicals from a number of kilometres away, yet residue amounts require shorter distances (i.e., <20m). Some of the algorithms that ChemImage uses assist in this process, as Dr Nelson explained. "You find with street drugs that the cutting agents can attenuate the signal of the narcotic. We counter that by adding to our library some of the cutting agents that you might find on the street so that allows the sensor to detect the narcotics as well. We can then utilise some spectral mixing routines in our algorithms to differentiate and pull out small constituents of the narcotics in the presence of those diluting cutting agents."

As with other sensors the substrate that the target rests on make some sensing difficult. Fingerprints on a knife blade or fentanyl in a bag is relatively easy, if it is hash oil on a brick then it is much more difficult. "Surface can have a negative impact especially if you are dealing with liquids on a porous substance like concrete then the liquid tends to wick away into the concrete and there's no material left on the surface. It is not as important if you are looking at solid residues. Absorption properties of the surface matter. If you are looking to get a response from a highly absorbent surface, it can attenuate the signal, the non-absorbing smoother surfaces tend to be the best, though we have had success with a wide range of substrate types," said Dr Nelson.

Like Raman, the shortwave infrared (IR) hyperspectral that ChemImage is using can sense through glass. As an added advantage over Raman it can do this from a significant standoff distance, while still being eyesafe. "The optical properties of the material will dictate what we can and can't go through, we can't go through metal or anything that would absorb all the light instead of being penetrated by it. We've taken lots of measurements through certain types of glass and plastic without a negative impact on detection. We have had success staring through vehicle windows and through glass vials with materials inside, so we can do that, but if the window is tinted there might be attenuation that can impact the detection performance."

This opens the possibility that VeroVision could be used at traffic stops, where suspects don't need to exit the vehicle and the visible elements of the car, both inside and out, can be quickly scanned for illicit substances. Currently the first prototype system is quite bulky,

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about 60lbs (27.2kg) with the powerpack and tripod, but in addition to the conformal version ChemImage is creating a handheld version that will bring greater capability and is improving the chemical, narcotic and explosive library. It won't be a silver bullet, low traces of agent are going to prove problematic, but the ability to do narcotic/chemical identification at a stand off distance will bring in the safety element that Dr Stokes talked about. It will allow categorisation of a crime scene to cue other detectors, such as Resolve, and it will also be more widespread in the law enforcement community than other CBRN sensors as it will have conventional forensic capability.

Moving from current state of the art in terms of Resolve and VeroVision we also have the prospect of future capability, albeit the near future. Hindsight Imaging[7] is another hyperspectral company, and according to their CEO, Arsen Hajian, they are bringing a change to threat imaging of an industrial revolution scale. Now, stop me if you have heard this before, but Dr Hajian is claiming to be able to deliver a complete Raman/reflectance hyperspectral capability in a package that is tens to hundreds of times smaller and at a price point around $10,000.

It's a big claim.

"I worked at the US Naval Observatory in the '90s, and made the discovery that allowed us to break the basic law of optics that correlates focal length and magnifications. It took me a long time to commercialise it, which didn't happen until 2010 after 15 years in development, however this means that we can build optical spectrometers using high-throughput virtual slit (HTVS) technology that are tens to hundreds of times smaller in volume without loss of performance. We are able to build engines that are pound for pound providing disruptively high performance in hyperspectral imaging. For some given application, say you need to detect something at a distance in a certain timeframe and at a particular level of confidence, then suppose the current technology needs a refrigerator size device to do that. We can rebuild that device with our HTVS technology, make it much smaller, have the same performance and sell it at the same performance in a much smaller package for a disruptively low price point."

Hindsight has had two thrusts into the market, the first was as an original equipment manufacturer, providing its HTVS for use in existing products, this has now ceased and they have re-invented themselves as a finished sensor manufacturer in its own right. As such Hindsight has produced four products[8], two are reflectance hyperspectral and two are Raman hyperspectral.

Dr Hajian is very enthusiastic about his technology. Through the hour's conversation his metaphors for the disruptive nature of his products build and build: "We have an engine that burns gasoline whereas spectrometer companies have an engine based on conventional technology that burns wood. We offer performance with few limiting tradeoffs. We are the first fundamental hardware reconstruction of a dispersive spectrometer since 1807, it is a hardware reconstruction rather than a laser that is 2% better. As a result, we measure improvement in factors of 10s of X."

Dr Hajian realises that his very enthusiasm can create concern in the market, but stresses that the more people get their hands on it the more they catch his bug. "There is blood and treasure on the line, we are not interested in selling sexed-up stuff, so we need to be clear about the limits. Any application where spectrometers are used in research environments, that would be the kind of business we take on. Our current customers include the Federal, State and local law enforcement forensics, we are looking at drugs in saliva and other bodily fluids, for example. Spectrometers currently exist in this space and we can make them much better. In 90% of the cases we can make our solution practical, but there are a few cases where we don't play well.

"When you talk about mass spectrometry or ion mobility spectrometry, some of them are very different from optical spectrometers and have advantages that spectrometers can't touch. Large pharma companies generate billions a year and two thirds of that is from nutrition in cereal box measurements. The common law is that, for certain jobs,you need a million dollar mass spectrometer. We are finding that we can make some of these measurements in under a tenth of second with our low-cost Raman systems. This is game changing technology for very large markets, but the problem we face is that a lot of people have claimed things in the past and now people look at us like we are offering a $5 Rolex. We beat every optical spectrometer, and a major portion of the Raman and reflection spectroscopy markets will be coopted by HTVS."

Thankfully, as with Dr. Nelson earlier, Dr. Hajian was on hand to explain the difference between hyperspectral Raman and conventional Raman. "We don't build point source spectrometers, instead we make an image of the scene to improve the quality of the detection. Suppose you wanted a chemical analysis of a human being in a swimming pool but not the water, a point source spectrometer would give you a spectrum of the swimming pool and the human all smushed together in one spectrum. Since the human being is only 1% of the scene the human would make a small contribution to the spectrum. In our case we make an image, which means that 99% of the pixels in the image are 100% water and one of the pixels is 100% human being, and that is how we talk about the contrast. When you do imaging your limits of detection get much higher but so do your costs. We have figured out how to contain those costs and build products that do imaging very well at price points that are interesting to many markets.

"Everyone else in the field of Raman imaging, for example, takes a point source and rasters it on the field. If you want to make a Raman image of something that is 1,000 by 1,000 pixels, then you need to make a million measurements. In our case we can use HTVS to create a line, so we are not illuminating the target with a point that we raster, we sweep a line across the source in one dimension and only make a thousand measurements. In addition to

the HTVS giving us an order-of-magnitude increase in performance, we get an additional large factor in performance by illuminating an entire line at once. There are no other commercially successful Raman imagers that light up the larget with line, everyone else uses a point, that allows disruptive performance."

As we discussed earlier in relation to Agilent and ChemImage, there is usually a tradeoff among range, limits of detection (i.e. detecting minute amounts of sample) and false readings – the smaller the trace amount, the higher the confidence of the detection, the closer you need to get. Dr Hajian also feels that his technology will bend, if not break, that correlation. "The HTVS technology allows new, practical ways of thinking. For example, you often get a lot of fluorescence that limits the return from the source, and anti-Stokes Raman gives you signals that are many times weaker, but there is no fluorescence. Nobody is eager to use anti-Stokes as Raman signals are already weak enough, but if HTVS can counteract that loss then suddenly we have opened up a whole area of Raman imaging that is florescence free. This is not about brute force, it is about using our capability to open up bottlenecks to allow established accoutrements, components and techniques in spectroscopy to have added powerand capability."

The initial growth of the company was fueled by sales of HTVS-equipped component spectrometer to selected customers, but customer demand for a full solutions made them change their plans. "About a year ago, we started getting demand from our Department of Defence (DoD) and security and defence customers for a full solution spectrometer for the detection of CBRNE solutions. We deployed two reflection spectroscopy solution products that are classic hyperspectral imagers, something that you might put on a drone and fly around. We also deployed two Raman solution products. The SpecVu is the reflection hyperspectral in a box and SpecVuR is the Raman system in a box. ChemVu is the same reflection system and ChemVuR is the same Raman system, but in an industrially-designed, handheld format. The reflective systems span the optical and near IR band, like everyone else with a silicon detector, and the Raman systems come equipped with a 785nm laser."

One challenge awaiting Hindsight, that Agilent has spent a long time grappling with, is library development. Based on what Dr. Hajian has claimed the HTVS, and affiliated systems, might be able to get a cleaner signal than many others, but it still has to have the spectra in the library to plot against. Historically there has been little tolerance for detectors that false alarm randomly, so this development of a bespoke library for a variety of agents, precursors and cutting agents is going to be a priority. It is one step at a time for Hindsight, and the team are working on six narcotics at the moment, with further agents expected down the line. "Fentanyl and the cannabinoid THC have no optical cross section – you could point a Death Star laser at those chemicals and they would be hard to detect. Silicon is also a pretty crappy detector if it is not cooled, so every Raman solution I have seen has a thermoelectric cooling system for the silicon chip. Fentanyl is the toughest of the six we are working on – heroin, cocaine, THC, MDMA and meth – and we can find it with an uncooled silicon detector.

HTVS increases the photon rate so much that, in some cases, you don't have to put a cooling system on our device, so the battery is measured in tens of hours, rather than single hours and its volume can be a lot smaller. I'd rather decrease the requirements of the onboard processing, decrease the power requirement and the device gets smaller by a factor of five to 10, and that has nothing to do with the spectrometer. Our on board processing requirements are much less than anyone else's and we have better limits of detection and lower false alarm rates simply because we have more spectral resolution. With the handheld device we can routinely get down to 10PPB on fentanyl in less than a second. By doing this we don't hand the engine off to someone else and ask them to figure out the implications in terms of cooling, algorithms, light source and battery, we do it all ourselves."

Dr Hajian's rhetoric tries to makes you believe that HTVS is going to be a game changer. Unfortunately no plan survives contact with the enemy, and any number of factors outside the technology could cause its vision to dissipate. The other element that offers a great deal of promise in the chemical/narcotic identification market, handheld mass spectrometry (MS), will be examined in the next edition. MS has been considered the gold standard for many years, and while that identification power might supersede Raman spectroscopy, whether SORS or HTVS, the inability of MS to be able to punch through containers/ surfaces, will mean that Raman and hyperspectral imaging will have an advantage in field operations for some time.

[1] https://onlinelibrary.wiley.com/doi/full/10.1002/dta.2300
[2] https://www.thermofisher.com/order/catalog/product/TRUNARC
[3] https://www.ecbc.army.mil/newspost/new-jcad-model-tests-for-opioids-illegal-drugs/
[4] https://www.agilent.com/en/technology/spatially-offset-raman-spectroscopy
[5] https://www.google.co.uk/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&ved=2ahUKEwjAqfWRn4PdAhUKyaQKHc9kAwQQFjAAegQIABAC&url=http%3A%2F%2Fopenroad.org.uk%2Fdownloads%2Flegalhighs%2FIan_Goldsborough_-_Public_protection_and_law_enforcement.ppt&usg=AOvVaw0w19ZafUtquFy5VQrUSXF9
[6] http://spie.org/Publications/Proceedings/Paper/10.1117/12.2223816
[7] https://www.hindsight-imaging.com/
[8] https://www.hindsight-imaging.com/wp-content/uploads/2017/11/Hindsight_Brochure.pdf