Surface analysis and hyperspectral imaging with quantum cascade lasers

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Invited Paper

Surface Analysis and Hyperspectral Imaging with Quantum Cascade Lasers

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Abstract

Block Engineering's pulsed external-cavity Quantum Cascade Lasers (QCLs) combine the optical brightness of lasers with very broad wavelength tuning to provide a breakthrough capability for spectroscopy. Over the past decade QCLs have been refined, become accepted as a spectroscopy tool, and applied to heretofore challenging sampling scenarios such as transmission through liquids or scattering off of low-reflectivity surfaces. More recent miniaturization of hardware and electronics are now enabling QCLs to become embedded in portable and hand-held instruments. This presentation will briefly review the current state of the art of QCL technology and describe systems recently developed for portable medical diagnostics and hyperspectral imaging.

Introduction

What is a QCL: Light sources can be used for various non-invasive probing measurements from gas detection to protein analysis and more. Measurement capabilities depend greatly on the choice of light sources, traditionally consisting of modest-power broad band emitters, or amplified laser emission at a single controlled wavelength[1]. A Quantum Cascade Laser, or QCL as they are often called, offers a way to combine these 2 capabilities into one very powerful solution. With the unique ability to sweep the output of a QCL through a range of wavelengths we have created a spectrally broad emission, typically in the IR spectrum. The ability to tune the output of a QCL provides the spectral brilliance of a laser with the flexibility of a traditional broad band light source[2]. Common QCLs have emission ranges on the order of 1-2 microns wide with a variety of center wavelengths in the Mid-IR spectrum, thus providing the flexibility of examining a wide variety of chemistries presented in samples in all phases of matter.

The theory of operation for QCLs dates back to 1971 when Rudolf Kazarinov and Robert Suris proposed the idea of a laser operating via intersubband transitions[3]. The operating principle included using a structure of repeated quantum wells to use tunneling from one transition state to another as the electron pump source. This idea lay dormant until 1994 when Federico Capasso and Alfred Y Cho at Bell Labs created the first functioning QCL[3]. This design would be further developed and refined as the field of semiconductor growth and epitaxy matures over the coming decades.

QCL operating principles: Today, QCLs are typically gown via MOCVD or MOVPE (Metal Organic Chemical Vapor Phase Deposition or Metal Organic Vapor Phase Epitaxy). These QCL structures consist of hundreds of layers of alternated active-inactive heterostructure semiconductors on the order of nanometer thickness. It is precise control over these layer thicknesses and material properties that determine the band structure and therefore, output wavelength of a grown QCL wafer[4]. The layer design of QCL wafers results in a repeated quantum well structure. Typically, these quantum wells are aligned in energy space allowing for

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the same energy state to be occupied in each. With the application of an electric field, these wells shift in allowed energy states. Electrons are then able to tunnel from a relaxed state of one well to an excited state of another well. Once in this excited state an electron can experience radiative decay to a relaxed state in that quantum well before tunneling to another. This mechanism is used as a replacement for traditional pump sources in more common lasing structures. Lasing efficiency can be further improved with the addition of an injector region to allow for a larger electron population. Figure 1 below shows an example of the energy structure of a QCL.

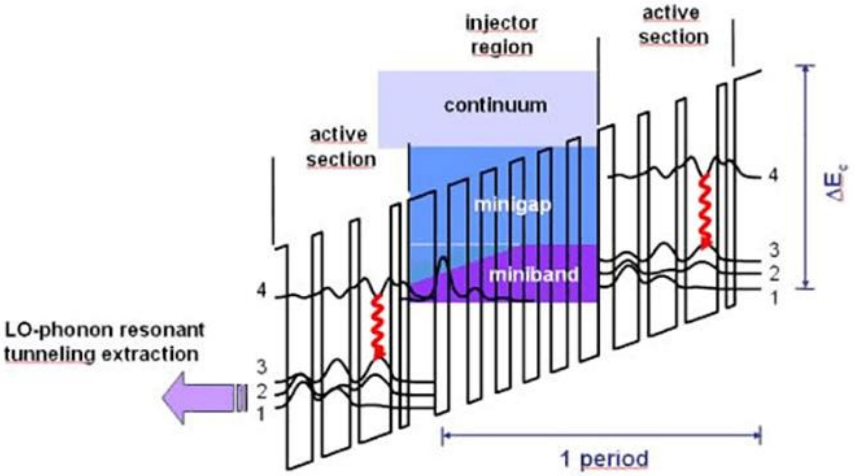

Figure 1: An example of the electronic band structure seen in modern QCLs[5]

While semiconductor growth has come a long way since the first QCL, the equally important external cavity optics, mounts, and housings of a QCL light source have made advancements as well. Current QCL housings, sometimes called tuners, are smaller, more robust, offer better thermal control and higher energy output as compared to early QCLs. The housing of a QCL is often responsible for maintaining stable operating conditions and selecting output wavelength. While output wavelength isolation can be achieved multiple ways, a very common method in commercial QCL systems is via diffraction grating. By rotating a diffraction grating relative to the light emitted by the QCL, specific wavelengths of light can be selected to exit the QCL tuner aperture. A QCL tuner comes into the limelight when the diffraction grating is made to move. While there are a multitude of ways in which the grating can be controlled there are 3 main functions that QCL tuners typically share: Sweep, Step and Single Wavelength. These options allow a user to “sweep” over many different wavelengths in rapid succession, “step” between and dwell on a series of discrete wavelengths, or select a single wavelength to output. Figure 2 below shows an example of a modern QCL tuner.

Figure 2: An example of a modern day QCL tuner produced by Block Engineering with programmable logic onboard so that it may be deployed with minimal supporting electronics.

Advantages of QCLs: QCLs offer many advantages over traditional light sources, the primary advantage is high optical output power compared to alternative Mid-IR options. Modern QCLs can offer peak output at powers as high as 350 mW in ranges from 5 microns up to 13 microns. These powers are achievable at room temperature with little thermal management required. Most modern QCLs can operate in ambient temperatures up to 30 degrees Celsius with minimal additional cooling hardware. Tuning range and wavelength control offer another advantage over traditional IR sources. QCLs are often able to cover 1-2 microns of tunable wavelength in a single tuner however, there are systems that are capable of combining many tuners to create tunable ranges up to 7 microns in width. Figure 3 shows an example of the Block LaserTune which is capable of tuning from 5.4 to 12.8 microns. QCLs are still a laser at heart after all and offer operation on short timescales with polarized and coherent light offering advantages in a multitude of measurements and applications.

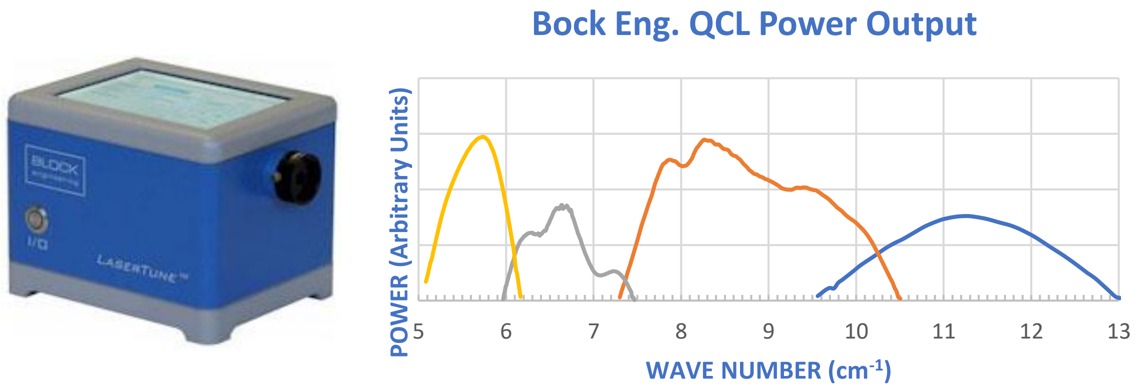

Figure 3: The Block Engineering LaserTune combines four QCL tuner and is capable of a gap-free tuning range from 5.4-12.8um

QCL historic uses and applications: While QCLs are a proven technology that delivers reliable, high power and tunable Mid-IR light, their uses historically have been limited over the past 2 decades to benchtop proof of concept style experiments due to size, temperature, power and portability considerations. In these setups QCLs have excelled in gas spectroscopy, protein analysis, AFM, surface imaging, hyperspectral imaging, security systems and various defense applications. However, these applications, while proven with QCLs, were stunted in commercial product integration due to the limitations listed above. We are now at the point where these limitations are behind us and the full potential of QCLs can be realized in fielded products.

Trials have shown that QCLs can be used to monitor gas concentrations during industrial processes. One example of this is work by The High Temperature Gas Dynamics Group at Stanford University. They showed that it is possible to measure the concentration of Nitric Oxide, an atmospheric pollutant, produced during industrial processes involving combustion. Nitric Oxide (NO) has a strong absorption band at 5.2 microns making it a prime candidate for detection using MIR sources. With a relatively short optical path length of approximately 18 meters, reliable detection of Nitric Oxide was demonstrated down to 0.3 ppm-m. A benefit gleaned from the use of QCLs for these measurements is the ability to measure the absorption of other chemicals simultaneously. By monitoring the absorption of NO relative to Carbon Monoxide or Water (with absorption lines at 4.6 and 7.59 um, respectively), the temperature inside the industrial process reactor could be determined[6]. This is a measurement that would not be possible with a traditional single wavelength laser therefore reducing the amount and complexity of measurement equipment needed for process control.

Due to the broad spectral output of QCLs they are uniquely suited to deconvolving complex gas mixes, an excellent example of this has been their use in demonstrating the viability of analyzing human breathe to aid in diagnosis. Through collaboration between the Laser Spectroscopy and Sensing Lab at ETH Zurich, the Life Science Trace Gas Research Group at Radboud University, and the Laser Science group at Rice University, the analysis of human breath using QCLs was brought to fruition. Through the infrared analysis of the relative presence a multitude of gases, diseases like Parkinson’s, Alzheimer’s and others can be detected. The analysis of human breath samples paved the way for advancements in other life science and environmental as well. QCLs offer a unique ability in ecological and environmental applications to monitor many different Hydro-Carbon based molecules at ppm levels offering precise monitoring of environmental processes[6].

Infrared Absorption Spectroscopy: The two applications discussed, as well as countless others, are at their core based on Infrared Laser Spectroscopy. Infrared absorption spectroscopy is a well-established phenomenon wherein infrared light interacts with gas and liquid substances and energy is imparted by the light to excite the molecular bonds and cause them to vibrate in one of several modes. The light absorptions occur at wavelengths which are characteristic of the unique binding energy of the excited bonds of the molecule. Thus, for each type of chemical there exists a unique infrared absorption spectrum, or fingerprint, which is determined by its characteristic molecular structure. The omnipresent FTIR laboratory devices, used for sample characterization, exploit this same phenomenon.

So, to characterize the chemistry of a substance you simply pass broad spectrum infrared light through the sample and look for which colors of light are missing to determine the fingerprint of the sample and thus its molecular composition. Practically speaking, this begins with a baseline measurement of the light source through the same optical path, but without the chemical sample to be interrogated. An example baseline measurement is shown in Figure 4 in which you can see the “raw” output of the laser, minus any absorption through the various optical components, and interpreted by a detector with its own non-linear detection sensitivities.

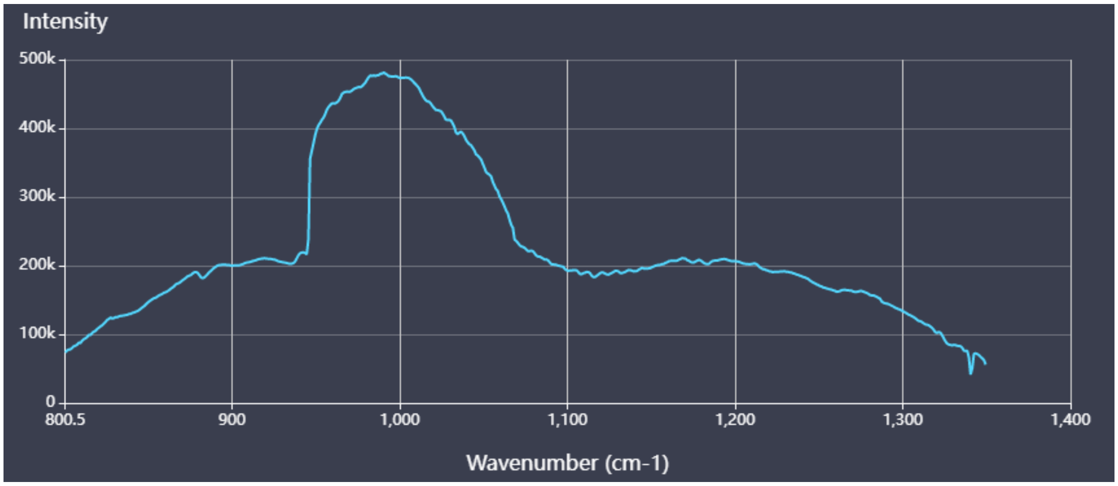

Figure 4: Baseline measurement for absorption spectroscopy. Measurements of the sample are then compared against this reference transmission curve.

After introducing the chemical sample to the optical path, the measurement is then repeated and compared to the baseline measurement. This produces the "transmission" curve shown in Figure 5. You will note that this shares the same general shape of the baseline measurement shown in Figure 4, but now includes the sharp dips in the curve, each dip corresponding to a specific molecular bond energy.

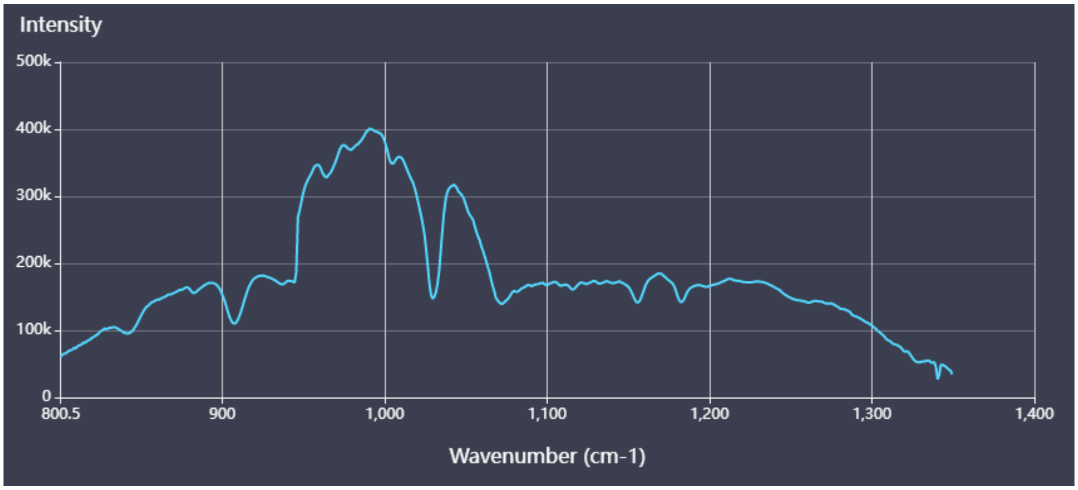

Figure 5: Transmission spectrum through the sample under test. Note the absorption "lines" which appear superimposed on the background spectrum above. The wavelength of each line is representative of a unique bonding energy and their combined presence constitutes the fingerprint of the molecule measured in the spectrometer.

The last step is to simply divide the background measurement from the sample measurement and we are left with an absorption spectrum which is normalized and much more straightforward to interpret. Figure 6 shows the resulting normalized spectrum containing fingerprint absorption lines of several unique chemical bonds. It then becomes fairly straightforward to compare the transmission spectrum against a collection of known fingerprints, and in this case, we determine the chemistry of our unknown sample to be Polystyrene.

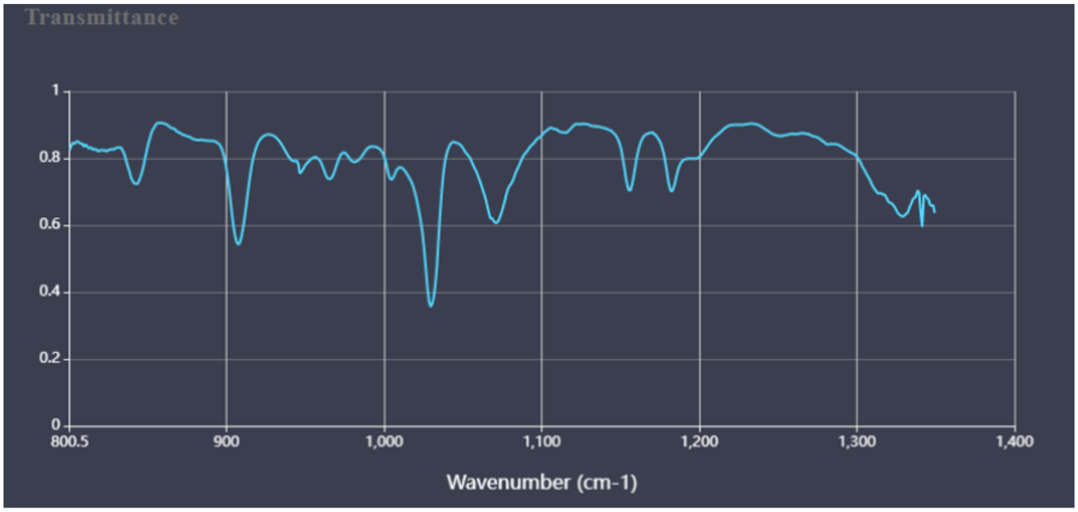

Figure 6: Sample transmission curve divided by the baseline measurement yields a normalized sample curve which we can compare against curves for known substances to determine the chemistry of our unknown substance.

This technique is regularly applied to gases or liquids and can be expanded from simple mono-samples to those containing several different molecular compounds. The approach is the same, but deconvolving overlapping fingerprints can be a challenge, so this becomes an excellent application for Artificial Intelligence algorithms. Further, since the molecular vibrations only absorb a small amount of light at the characteristic wavelength, the light can pass through a multitude of molecules without being completely attenuated. Thus, the strength of the absorption at a given wavelength can also be used to determine the concentration of the detected chemistry (after calibration with known samples).

New advancements, particularly in QCL form factor, have opened the door for many applications to be commercialized. With QCLs sized to fit in the palm of your hand, rather than a shoe box, and electronics that enable application specific laser programs to run autonomously without supporting electronics, the opportunity for mobile or even hand-held systems has arrived. One such industry that has benefited from more compact QCLs is security and defense. With systems that can be powered by battery and deployed in the field, stand-off chemical detection is being revolutionized and brought into the 21st century.

Modern QCL Applications

Gas Detection Application of QCLs: Gas detection based on the unique infrared signatures of infrared molecular absorption is a well-established technique that has been deployed for many decades. Such systems are in widespread use in ensuring building air quality (e.g. CO, CO2), auto emissions (e.g. CO, NOx), and medical diagnostics (e.g. CO2) to name a few. Simplistic versions of these systems are typically based on monochromatic LEDs when the application requires only single gas detection and background is well understood. When a full spectrum is required, then broadband light sources are required to provide a wider range of wavelengths and more complete spectral information. Traditionally these spectrometers utilize an incandescent light source consisting of a heated ceramic or tungsten filament bulb. These sources provide a nice broad spectrum, but are limited in power output. Thus, until recently, gas sensors have been limited to short range measurements with moderate limits of detection. The development of QCLs to provide broad spectral light coupled with the inherent power of the laser has opened up numerous applications that were previously not addressable with broadband infrared technology.

A great example of long-range gas detection is Block's LaserWarn product which projects a powerful QCL beam of light over several hundred meters to detect gases in large open spaces such as building lobbies, transportation stations, and along fence lines. A retro-reflector is placed on the far side of the area to be monitored and serves to return the collimated beam back to the instrument, and small flat mirrors can be used to direct the beam around corners or traverse a lobby to create the desired pattern of coverage. With this beam of light and the known absorption spectrum of individual gases, we are able to detect gases which are introduced into the path of the laser and thus identify and quantify atmospheric gases that are present between it and a retroreflector placed at standoff distances of up to 300 meters. Figure 7 shows the concept:

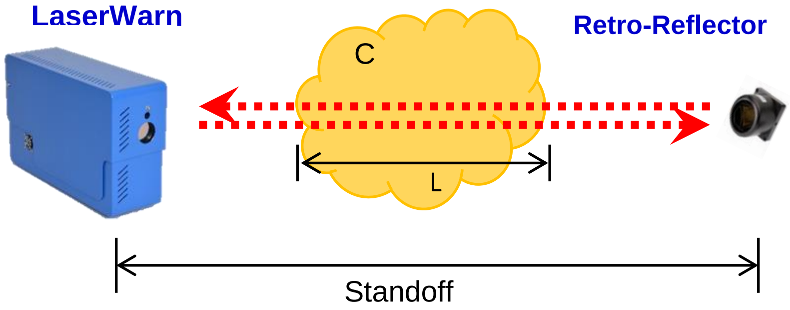

Figure 7: Visualization of the LaserWarn's Concept of Operation. Broadband Infrared light is directed across an open path and returned to the instrument by a retro-reflector. Any gas intercepted by this beam will absorb at characteristic wavelengths and thus be readily identified by the instrument's AI algorithm.

In accordance with the Beer-Lambert Law, the detection capability is determined by the concentration of the cloud (C in Figure 7) times the length of the cloud (L). It utilizes QCLs to generate a collimated beam of light (wavelengths 7.5 – 13 µm) that can be rapidly tuned in wavelength across the LWIR. This is the powerful "fingerprint" region and nearly all chemical warfare agents and toxic industrial chemicals have strong features in this region. Highly sensitive ppm detection limits can be achieved because the mid-IR absorption coefficients are typically very large and the optical path lengths can be very long. Because the system is compact and requires no consumables it is a practical solution which can be installed in many environments where a threat of attack exists; Figure 8 depicts an example installation.

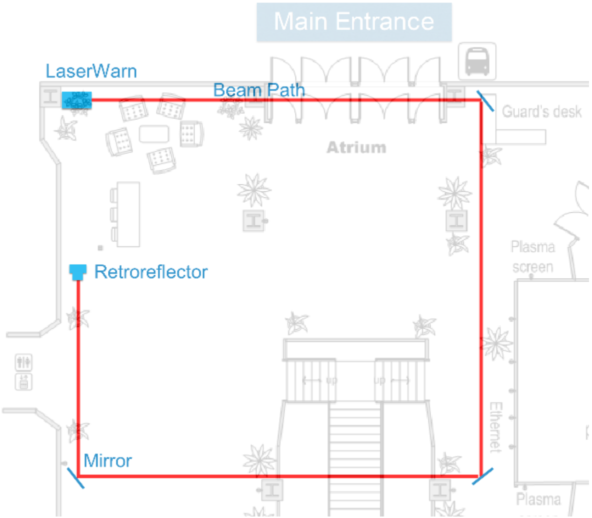

Figure 8: Example LaserWarn Installation in a building lobby to create an invisible trip wire detector which provides early warning of gas releases.

Surface Interrogation Application of QCLs: Taking an airplane trip provides a great example of today's state of the art in surface interrogation. Carry-on luggage or people that draw the attention of the Transportation Security Administration (TSA) at the checkpoint are pulled aside for inspection. As part of this inspection a swab is wiped across various surfaces and presented to an Ion Mobility Spectrometer (IMS) for inspection in TSA's hunt for explosive materials. This process takes an average of 6 minutes, and requires that the security agents touch you and your carry-on materials. In our new Covid world, the TSA agents would (understandably) rather not be forced to touch things or people, and maintaining the rapid flow of passengers through the check station is of critical concern to all involved. What if this important screening could be conducted in a few seconds and not require any contact at all?

The latest, and perhaps most innovative, application of QCL technology is in optically determining the chemistry of trace residue on surfaces without contact. To accomplish this, our miniature QCL lasers are combined with LWIR cameras to create Hyperspectral Imaging (LWIR-HSI) systems (called LaserScanTM) that can map out chemical contamination to localize fingerprints, smears, particles, etc., with a spatial resolution of better than 1 mm. These systems have proved to be highly effective at detecting and identifying trace chemicals and in particular explosives, CWAs, and drugs (similar in composition to fentanyl and other opioids) on a wide range of substrates. Results can be presented in the form of a so-called "detection map" as shown in Figure 9.

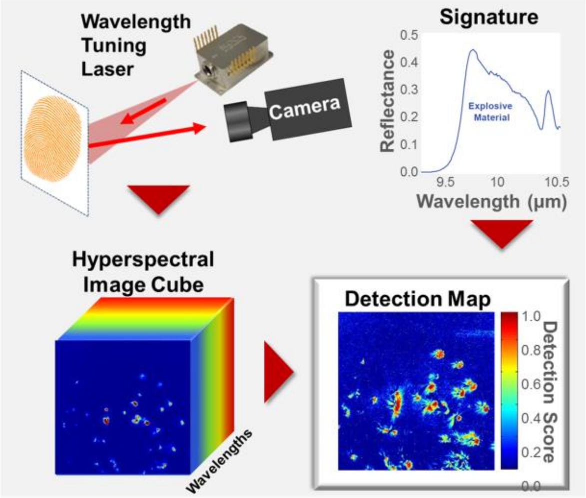

Figure 9: Concept of laser-based LWIR Hyperspectral Imager (HSI) for trace chemical detection. The HSI cube of spectral data overlayed on surface images yields a very powerful trace detection map.

The basic idea of our approach is to measure the reflectance of a wavelength tunable quantum cascade laser (QCL) off a surface as a function of wavelength in the LWIR. The QCL illuminates the surface of the target (e.g. hands, cell phone, jacket, parcel, shoes, laptop, etc.) and the reflected light is imaged using an IR camera. While the laser wavelength is swept through the mid-infrared, the camera captures an image of the reflected light at each wavelength to build up a so-called hyperspectral image cube (i.e., hypercube). This hypercube is then analyzed using advanced algorithms to detect, identify, and map any trace chemicals by comparing the measured spectra with a library of spectra. Specialized algorithms account for and eliminate the spectral effects of the surface on which the trace explosive particles reside.

This innovative inspection technique is finding applications in screening large numbers of people, vehicles, packages etc. at high speed. Using Machine Learning (ML) algorithms, the data collected by the hyperspectral imager is able to be rapidly compared to a library of anticipated substances and through statistical matching we are able to identify substances on the surfaces interrogated. The ML analytics have evolved to the point where combinations of chemicals can be spectrally deconvolved and identified by the constituent chemistries. This is a very powerful capability in the chemically and temporally challenging field of security.

Conclusion: Quantum Cascade Lasers have seen several decades of refinement and application development, and through this process have become a truly mature technology and proven very useful in a host of applications from sample analytics to process monitoring and laboratory instrumentation. As with any emerging technology, the timeline from invention to practical application and finally refined utilization can be arduous. With QCLs we are finally at the point where the technology is robust and the thought leaders in various industries have accepted the QCL as an established technology solution which is ready for deployment, of which this article cited numerous examples. Now with the further evolution of QCLs to run as miniature modules independent of supporting electronics, and at a relatively inexpensive price point, we are now launching into a new world of hand-held instrumentation worthy of field deployment in volume. It will be interesting and exciting to see all of the innovative portable applications that this new capability will facilitate over the coming decades.

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