

A New, Hand-Held, 1 to 5 m Standoff Analyzer for Real-Time Detection of Trace Chemical, Biological, and Explosives Substances on Surfaces

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Abstract

Real-time assessment of suspicious substances on surfaces is an important capability needed by warfighters/first responders. It is also important to perform these assessments without contact or spreading of the suspicious substance or use of reagents. We present work conducted under DTRA and Army funding to develop a hand-held, 1 m to 5 m standoff, optical sensor which detects and classifies trace and bulk concentrations of a wide range of chemical, biological, and explosives (CBE) materials in real-time and full daylight with a fully integrated analyzer weighing less than 12 pounds, including batteries.

The sensor method described here combines the complementary chemical information of molecular bonds using Raman and the electronic configuration information using fluorescence, with excitation below 250 nm. There are six main advantages of excitation below 250 nm compared to near-UV, visible or near-IR counterparts: 1) Solar blind detection enabling standoff operation in full daylight; 2) Fluorescence-free Raman and Raman-free fluorescence enabling enhanced detection and identification of target materials without mutual interference; 3) Resonance Raman signal enhancement for improved Raman sensitivity; 4) Simplification of Raman spectra due to resonance enhancement, 5) Short penetration depth, providing physical separation of surface contaminant materials from substrate; and 6) Eye retina safe. These detection capabilities are not possible with near UV, visible, or near IR sensors. A special feature of our sensor is the ability to detect trace biological materials at standoff distances in real time.

Photon Systems and JPL have developed these methods over many years, enabling instruments deployed to extreme environments on Earth and an upcoming lander mission to Mars in 2020.

Keywords: standoff; hand-held; deep UV Raman; native fluorescence; chemical; biological; explosives; detection; classification;

1. INTRODUCTION

Real-time, in situ, assessment of suspicious substances on surfaces is an important situational awareness capability needed by warfighters and first responders. It is also important to be able to perform these assessments without contact, disruption, or spreading of a suspicious substance or use of reagents. This is important for the safety of first responders. This paper presents the status of work conducted under DTRA and Army funding to develop a 1 m to 5 m standoff, hand-held, optical sensor which can detect and classify trace and bulk concentrations of a wide range of chemical, biological, and explosives (CBE) materials in real-time and full daylight conditions with a single, fully integrated, device weighing less than 10 pounds, including batteries. We call this sensor a Standoff Handheld CBE (SHCBE) sensor.

Present hand-held COTS surface contamination sensors predominantly employ visible or near IR Raman methods, which are not usable in daylight conditions except when in essential contact with the suspicious powder. They are also limited in the number of detectable chemical & explosive materials because of Raman signal interference by fluorescence or sample burning and are essentially unable to detect biological substances. Biological detection is presently limited to methods that require collection of samples to be used with immunoassays or PCR, both of which require bulky and expensive equipment and expensive reagents with limited shelf life and restrictive environmental conditions for storage and use. Other hand-held sensors such as PID, FID, IMS, and MS sensors detect airborne gases and vapors, which may be a result of natural or forced evaporation of surface material. But they do not detect substances on surfaces which have low vapor pressure unless released by thermal desorption or similar methods, normally conducted very near to the sample. Deep UV Raman spectroscopy is an emerging sensor technology that can also include native fluorescence from samples to provide many detection benefits over near UV, visible, and IR Raman methods. Although these concepts have been

demonstrated over thirty years ago [1], it has only emerged as a potential method for hand-held or man-portable applications in the recent past.

2. DESCRIPTION OF THE SHCBE ANALYZER

The SHCBE 200 Analyzer is the first and only fully integrated real-time deep UV Raman and fluorescence analyzer instrument, providing complementary and confirmatory spectroscopic testing in a single handheld device.

Identify a wide range of unknown chemical, biological, and explosive materials on surfaces at standoff distances of 0.5 to 5+ m, in the field, in real time, and in full daylight conditions in a single, hand-held instrument. The Photon Systems SHCBE 200 analyzer employs two complementary optical methods, deep UV Raman and fluorescence spectroscopy, without any optical interference from ambient light or due to Raman and fluorescence spectral overlap.

SHCBE 200 is a fully self-contained hand-held point-and-shoot analyzer with ATAK and MFK compatibility which contains a deep UV laser and control electronics, built-in-test with auto-calibrating spectrometer, autofocus telescope for targets from 0.5 to 5+ m, single handed control, wide and narrow field of view context images, and embedded computer with on-board data processing with CBE library and display showing context information and target identification.

Many detectors suffer from poor sensitivity and/or incorrect identification due to the use of only one detection technique. The SHCBE 200 is the only standoff handheld detector to utilize both deep UV Raman and fluorescence. This gives the SHCBE 200 unsurpassed sensitivity and specificity for detecting a wide range of chemicals, explosives and biological agents. NASA/JPL is using this same technology on Mars to detect organic compounds with SHERLOC detector on the Mars 2020 rover.

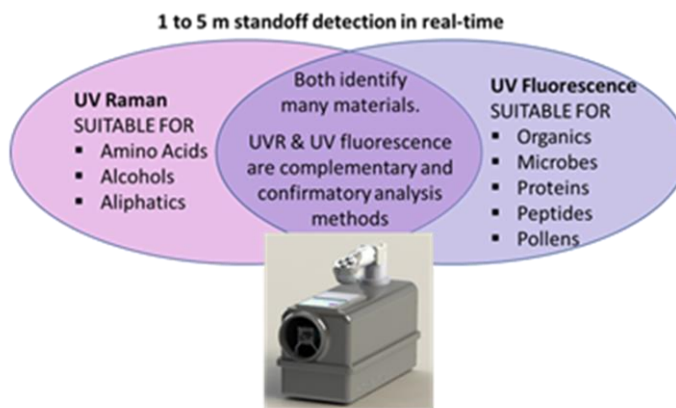


Figure 1. Multi-mode SHCBE analyzes a wide range of compounds

SHCBE 200 FEATURES

- **Single handed operation:** 4-button plus trigger control
- **Warm-up:** < 10s from cold start, 3 s from standby mode
- **Built-in-test:** full functional test of all components on startup
- **Spectral Calibration:** Auto-calibrated on analyzer startup
- **Two Coaxial Context Cameras:**
 - 75 degree wide angle image
 - 20 mm close up image centered on laser spot
- **Autofocused Standoff:** based on micro context image
- **Standoff Distance:** 0.5 m to 5+ m in full daylight conditions
- **Spectral Range:**
 - Raman:** 250 cm^{-1} to 4000 cm^{-1}
 - Fluorescence:** 270nm to 320nm
- **Materials Detected:** Chemical, Biological and Explosives
- **CBE Libraries:** Built in unclassified library +SD card libraries

OTHER INFORMATION

- **Context Info with Spectral Data:** Date/time stamps, GPS, azimuth, distance and two images
- **Power Supply:** Replaceable 24 V LiPO battery pack (UN/DOT 38.3 rated) or 24 V wall adapter
- **Communication:** WiFi/Bluetooth (to Android/ATAK), plus Wired USB 3.0
- **Weight:** 10 pounds
- **Dimensions:** 7" W x 11" H x 16" L
- **Battery Lifetime:** >20 hrs in standby, > 200 spectral analyses
- **Display:** Color 1920x1080, 5.9" LCD
- **Ambient:** -40 °C to +60 °C, 0-90% humidity, -1 km to +20 km
- **Shock/Vib:** TBD
- **Ingress Protection:** IP65
- **Robot compatible:** ¼ -20 camera thread or dove-tail mount
- **Maintenance:** > 1 year with window clear of debris

3. BENEFITS OF DEEP UV RAMAN & FLUORESCENCE DETECTION

The SHCBE Analyzer described here uses a fusion of Raman and fluorescence emissions excited in the deep UV. Raman spectroscopy provides information about molecular bonds within a targeted substance, while fluorescence spectroscopy is over 1 million times more sensitive than Raman and provides information about the electronic configuration of target molecules, including ring structure & side chains. This enables detection at longer distances and lower concentrations. Both modes of spectroscopy provide orthogonal and complementary information about an unknown material and increase the overall probability of detection and decrease false alarm rates. The extreme sensitivity of fluorescence enables fluorescence to be a rapid search tool followed by the much slower Raman for further chemical confirmation. There are seven important advantages of excitation in the deep UV compared to near-UV, visible or IR counterparts.

- 1) Excited in the deep UV below 250 nm, Raman emissions from targeted materials occur in a spectral region devoid of interference from solar/stellar or artificial lighting, enabling detection at standoff distances in full daylight or artificial light environments. Fluorescence emissions are solar blind up to about 320 nm, a spectral region occupied by the most ubiquitous materials found in nature.
- 2) Very few materials have any fluorescence emission below about 275 nm [1], independent of excitation wavelength. When excitation occurs below 250 nm, Raman emission occur within a fluorescence-free region of the spectrum between the excitation wavelength and about 275 nm, eliminating obscuration of weak Raman signals by fluorescence from targeted or surrounding materials. This is illustrated in Fig. 2 a & b, where the Raman spectral region is on the left and fluorescence spectral region in on the right, both excited at 248 nm. No baseline compensation needed.
- 3) Because Raman and fluorescence occupy separate spectral regions, detection can be done simultaneously, providing a much wider range of information about a makeup of a target substance [2,3,4,5].
- 4) Rayleigh law and resonance Raman effects increase Raman signal strength and sensitivity of detection.
- 5) When excitation is below 250 nm, fluorescence emissions from the smallest and most ubiquitous compounds are excited over the full spectral range of the material, without alteration by strong Raman bands. This enables identification information, especially of biological materials.
- 6) Penetration depth into target is very short when excitation is in the deep UV, providing physical and spectral separation of a target material from its background matrix or surrounding material.
- 7) Non-contact: no sample contact, handling, disturbance, spreading, or alteration.

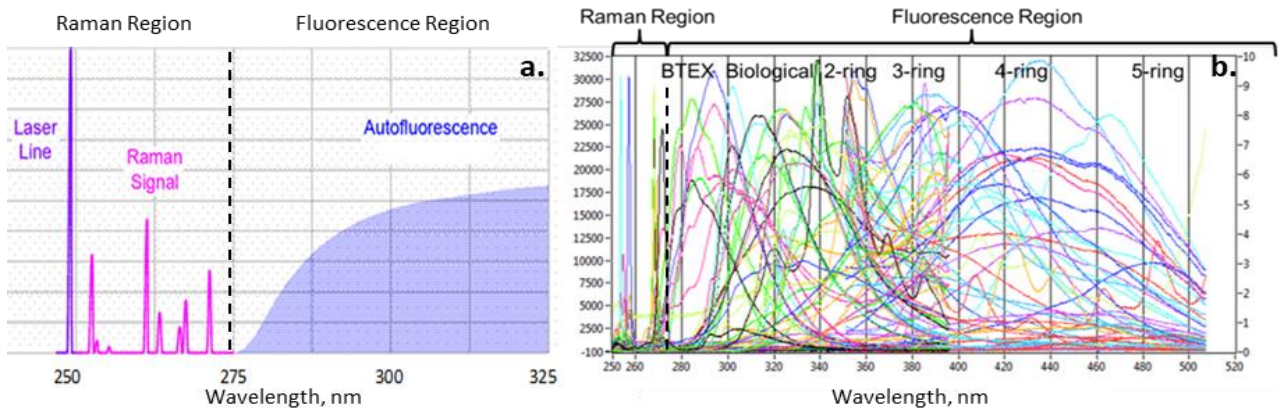


Figure 2. Separation of Raman & fluorescence spectral regions with 248.6 nm excitation: Left-amino acids; Right-broad range of organic material. Excitation at 263 nm causes obscuration of major Raman bands of many important materials by fluorescence.

4. RESULTS

The SHCBE Analyzer is an evolution of earlier sensors, all of which employ both Raman & fluorescence methods for detection and classification of unknown substances on surfaces. The present SHCBE evolution has the same Raman spectral resolution and better fluorescence spectral resolution compared to these predecessors, and therefore, we expect similar to superior results.

Because of the unique ability of SHCBE to detect and classify trace concentrations of microbial material, the first examples shown below are of biological detection. Figure 3 shows mapping of trace microbial material, at a concentration less than 10^6 cells/cm², smeared on an off-white painted wall in an office, with the materials being two, gram negative, genera (*E. coli* and *S. oniedensis*) plus a smear of tryptophan. Data for each spatial element was taken at a standoff distance of 2 m during a single 50μs pulse from an NeCu laser at an excitation energy about 5 μJ. The color of the different microorganisms is NOT artificial, but a result of assigning the first three principal components of PCA analysis to Red, Green, and Blue intensities. Thus, the color variations are a legitimate

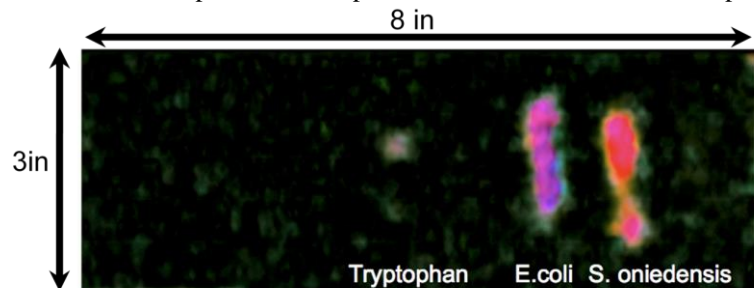


Figure 3. Chemical mapping of trace microbes on painted wall Detector standoff at 2 m with data from each spatial element taken in 50 μs at an excitation energy about 5 μJ.

representation of the chemical composition difference between these organisms.

Another microbial detection illustration is shown in Fig. 4, where the ability to differentiate several different organisms based on their deep UV fluorescence spectra processed using Principal Component Analysis (PCA) is shown [6]. Under an Army SBIR Contract No. W911NF-14-C-0142, we demonstrated the ability of our deep UV method to detect biological material down to a single bacterial spore and the amount of biological material corresponding to a large virus using our deep UV fluorescence spectroscopy and microscopy on natural and opaque substrates without the need to tagging or sample handling. We demonstrated that a suspicious powder on a surface (with focus on microbial powder) can be detected and classified not only into whether it is bio or non-bio, but also what class of biological material, such as microbe, protein, or plant or skin cell, and further classified to whether the powder is a bacterial cell or spore, a yeast, a fungus, or a fungal spore, and finally, classified into the rough species of the bacteria. And this can be done when diluted in talc or other inert material at up to 70,000:1, detecting as few as 5 bacteria within the sensor view. It has also been demonstrated that this sensor can be further used to detect and classify a much wider range of non-biological material including a wide range of chemical and explosives materials, as described above.

The deep UV spectroscopic data are collected and processed using Principal Component Analysis (PCA) where the PCA eigenvectors are iteratively trained to focus on smaller and smaller sets of the overall training data, through a 4-level triaging process. The overall PCA training set includes chemical, biological, and explosives data. Although the method appears to measure a combination of genotypic and phenotypic information about microbes, it was shown that different microorganisms show measurably different fluorescence spectral characteristics, since the spectra are a result not only of the inherent chemistry within a microorganism, but also due to the conformation and configuration of that chemistry within the microorganism, and the inherent shadowing and interaction of and by the basic chemical ingredients.

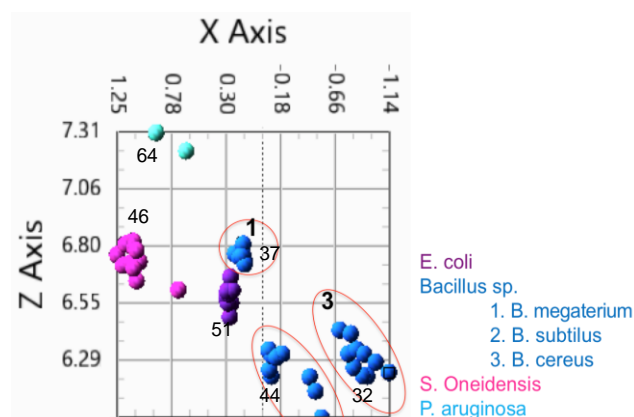


Figure 4. 4th level of triage iteration. GC% noted by groupings

Figure 4 shows the level of spectroscopic separation possible for different bacterial species and other microbes using deep UV fluorescence alone. This differentiability is at level four of the iterative PCA sample triage process. It suggests that a very high level of differentiability, even of trace concentrations, of a suspicious material, especially focused on biological material but also including chemical and explosives, can be accomplished using a small, hand-held, lightweight, reagentless, non-contact sensor, in less than a few seconds. While this sensor is not a definitive biological confirmation sensor, such as can be provided by PCR, it is a high-level trigger sensor that can detect and classify a wide range of suspicious powders in less than a few seconds, at the site of an event, without the need for sample handling, processing, or use of reagents.

In addition, DTRA sponsored independent testing of the TUCBE 4.5 detector developed under contract with them (HDTRA1-09-C-0010). The Targeted Ultraviolet CBE Sensor, Gen 4.5 is a predecessor of the present SHCBE 200 sensor described above. Both instruments have the same Raman spectral resolution but the new SHCBE 200 instrument has much higher fluorescence spectral resolution. Other benefits of the new SHCBE sensor is that it is much smaller and lighter than its TUCBE 4.5 predecessor, while also featuring a longer-range telescope for extended standoff performance from 1 m to 5 m in full daylight or artificial light conditions.

Tests were conducted on: 1) Chemical Warfare Agents (CWAs) and Non-Traditional Agents (NTAs) at ECBC in Edgewood, MD; 2) explosives and ingredients at Indian Head Explosives Ordnance Detection Technical Division (IHEODTD) at Indian Head, MD; 3) and on biological agents at three locations including at IHEODTD at Indian Head, MD, at University Microspectral Laboratory (UML) at Ponca City, OK, and at Lawrence Livermore National Laboratories (LLNL) at Livermore, CA. Some of the results for testing of CWAs and NTAs at ECBC will be described below as well as for explosives testing conducted at IHEODTD. Results of biological testing at UML, LLNL, and IHEODTD have not been released to the public.

CWA & NTA Testing at ECBC

A translation matrix was used between ECBC and Photon Systems to compartmentalize the data. This prevented direct associations between the spectra (which are unclassified) and the agent analytes' identity and structure per decision of the government agencies involved in the testing. Though this arrangement did not allow Photon Systems to inform their principal components analysis methods proactively, we still could measure chemical clustering based on molecular structural similarity to other reference materials in a device library and we provided that information to ECBC.

Using the Photon Systems' TUCBE 4.5 detector, ECBC conducted independent tests on nine (9) different CWAs and NTAs in two primary conditions: nine (9) pure CWAs and NTAs in fused-silica cuvettes; and a subset of four (4) CWAs and NTAs on three (3) different surface types. ECBC provided Photon Systems with two different coded deep UV Raman & fluorescence data sets: one set of 24 blind, unknown, samples, designated UN01 through UN24; and one set of coded library data on the pure samples, designated A through I on three surface types, designated S1 through S3. The goal was for Photon Systems to demonstrate that the TUCBE 4.5 could accurately identify the 24 unknown samples using the coded library.

Table I below relate the 24 unknowns to coded samples. The results include CWAs and NTAs pure, on surfaces, and the surfaces alone. Since this was a blind test, the real identities of the unknowns were known only to ECBC until submission of Photon Systems' results. Photon Systems submitted the coded identity of all 24 blind unknown samples to ECBC along with the confidence of the match of the unknown and the Raman and fluorescence library data, based on the Euclidian distance between unknowns and library data, measured in Principal Component Analysis space, for Raman and fluorescence data used in separate analyses. The ECBC identification results are also shown in Table I.

Column 1 lists the 24 unknown samples. Column 2 shows the best match from Photon Systems/JPL analysis of the coded data along with confidence of the match for florescence and Raman data in columns 3 and 4. Column 5 is the ECBC verification of our column 2 results, provided after our analysis was finished. Columns 6 & 7 summarize the results.

Table I. ECBC deep UV Raman & fluorescence chemometric matching with library data

1	2	3	4	5	6	7
Unknown Sample	Matched Material (PSI/JPL Analysis)	Fluorescence Match (%)	Raman Match (%)	ECBC Actuals	Correctly Identified Chem	Correctly Identified Surface
UN01	F_S1	99.44	99.77	F_S1		
UN02	S2	99.93	99.78	S2		
UN03	C_S2	99.95	99.76	C_S2		
UN04	D_S2	99.04	99.67	D_S2		
UN05	E	99.94	99.73	E		
UN06	A	99.86	99.87	A		
UN07	B_S2	95.99	98.76	B_S2		
	UN22	98.35	98.86			
UN08	C_S3	99.94	99.78	C_S3		
UN09	F_S3	92.84	98.43	F_S3		
UN10	H	99.95	99.85	H		
UN11	G	99.96	99.88	G		
UN12	F_S2	96.63	99	F_S2		
UN13	C	99.63	99.8	C		
UN14	D	99.93	99.73	D		
UN15	S1	99.84	99.76	S1		
UN16	B_S1	99.29	99.63	B_S1		
UN17	F	99.97	99.7	F		
UN18	I	99.79	99.73	I		
UN19	S3	99.57	99.62	S3		
UN20	C_S1	99.55	99.76	C_S1		
UN21	D_S3	99.88	99.72	D_S3		
UN22	B_S2	94.35	97.85	B_S3		
	UN07	98.35	98.86			
UN23	B	99.73	99.83	B		
UN24	D_S1	99.62	99.77	D_S1		

In summary, among the 24 unknown samples, 100% of the 9 pure samples were correctly identified with a minimum confidence above 99.63%. Among all 24 blind unknown samples, the match was above 97.85% for Raman matching and above 98.35% for all but 4 unknowns, where the confidence was 96.63%, 95.99%, 94.35%, and 92.84%. The lower confidence matches with library results were due to weak signal strength on unknown, but trace, concentrations of analyte on surfaces. While for the most part, the fluorescence and Raman both have high similarity values, the fluorescence is slightly less accurate than the Raman for a few samples. This appears to be more specific to the specific chemical (B and F) rather than any other factor.

Explosives & Ingredients Testing at IHEODTD

Thirteen (13) military grade and home-made explosives and key ingredients were independently tested using a TUCBE 4.5 detector at IHEODTD at Navy Stump Neck, Indian Head, MD. These results are shown below in Table II.

Table II. Military and homemade explosives and ingredients detection.

	False Positives	False Negatives	Correctly ID'd	N values
Perchlorate	0%	0%	100%	2
Chlorate	0%	0%	100%	2
Ammonium Nitrate	0%	0%	100%	10
Urea Nitrate	0%	0%	100%	1
ANFO	0%	0%	100%	4
Black Powder	0%	0%	100%	6
Smokeless Powder	0%	0%	100%	1
Hydrogen Peroxide	0%	50%	100%	2
Hydroxides	0%	0%	100%	3
C4	0%	0%	100%	7
PE4	0%	0%	100%	4
PETN	0%	0%	100%	11
TNT	0%	0%	100%	11

The 50% false negative value for hydrogen peroxide was due to the low signal to noise value.

5. EXTENSIONS OF SHCBE TECHNOLOGY

Two extensions of the SHCBE technology are illustrated below: a proximity version of the SHCBE 200, called the SHCBE 125, and SHERLOC, a rover-arm-mounted deep UV Raman & fluorescence instrument using many of the same elements as SHCBE, but for detection of trace organic, prebiotic, and biological materials on Mars.

The primary differences between the SHCBE 200 and 125 are the standoff distance and the instrument size and weight. Both instruments share the same laser and detection methods and have the same software, display, and communications. The nominal SHCBE 125 spec is shown below along with two illustrations.

SHCBE 125 Specifications:

- ✓ Detection type: fused deep UV Raman & fluorescence
- ✓ Laser wavelength: 248.6 nm
- ✓ Auto-Focus working distance: 4 cm
- ✓ **Bump test calibration:** Raman & fluorescence spectral and amplitude
- ✓ Sampling size: < 0.5 mm dia
- ✓ Detection time: < 100 μs for Raman & fluor
- ✓ Sensor warmup time from cold start: < 10 s
- ✓ Size: 4"x7"x14"
- ✓ Weight: < 5 lbs, including battery
- ✓ Battery life: > 16 hours typical
- ✓ Environmental: IP67
- ✓ Command/control/display: large membrane switch control + OLED
- ✓ Alternate command/control/display: via Android phone, ATAK, etc.
- ✓ Context camera with image captures with data sets
- ✓ On-board CBE library



Figure 5. Specifications and illustration of SHCBE 125

The second extension of the SHCBE technology is an instrument called SHERLOC (Scanning Habitable Environments using Raman & Luminescence for Organics & Chemicals”, a Mars 2020 Rover-arm-mounted instrument planned for launch to Mars in August 2020.

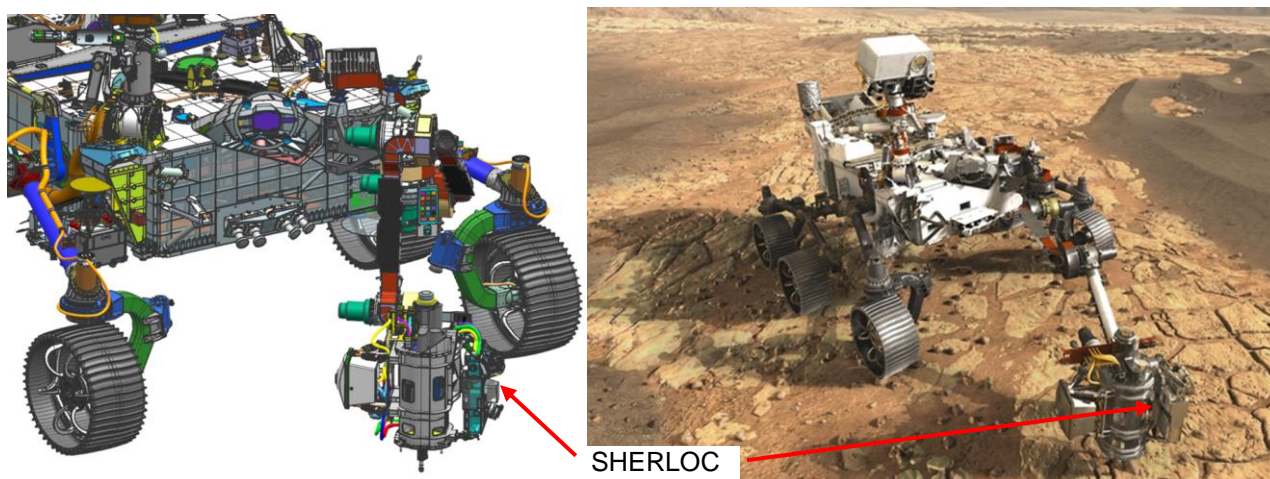


Figure 6. Illustrations of the deep UV Raman & fluorescence instrument, SHERLOC, on the distal end of the arm

6. SUMMARY

In the world of light weight handheld field instruments SHCBE is unique: real-time; 1-5 m standoff in full daylight; wide range of chemical; biological; and explosives materials; and designed to protect first responders. SHCBE has been demonstrated to be able to accurately detect a wide range of C, B, and E materials in independent testing at government laboratories.

Present hand-held surface contamination sensors predominantly employ visible or near IR Raman methods, which are not usable in daylight conditions except when in essential contact with the suspicious powder. They are also limited in the number of detectable chemical & explosive materials because of Raman signal interference by fluorescence or sample burning and are essentially unable to detect biological substances. Biological detection is presently limited to methods that require collection of samples to be used with immunoassays or PCR, both of which require bulky and expensive equipment and expensive reagents with limited shelf life and restrictive environmental conditions for storage and use. Other hand-held sensors such as PID, FID, IMS, and MS sensors detect airborne gases and vapors, which may be a result of natural or forced evaporation of surface material. But they do not detect substances on surfaces which have low vapor pressure unless released by thermal desorption or similar methods, normally conducted very near to the sample. SHCBE is uniquely qualified to fill this application niche.

7. ACKNOWLEDGEMENTS

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