Contract No:

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LDRD-2018-00098
LDRD External Report Summary

Hyperspectral Raman Imaging using a Spatial Heterodyne Spectrometer (SHS)

Project highlight. Savannah River National Laboratory, and the larger community, has limited chemical-specific imaging capabilities, which would be beneficial for remote detection of threat chemicals or use in inaccessible and harsh environments, as well as in-line process monitoring. The project objective is to develop a novel, rugged, highly sensitive spectrometer to support real-time, chemically specific imaging using hyperspectral Raman spectroscopy.

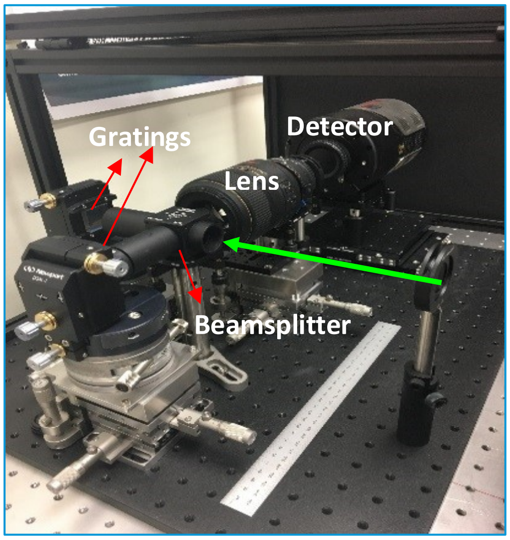

Figure 1: Image of SHRS built at SRNL. Green arrow indicates incoming light.

Awards and Recognition

NA

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publicly published in its current form.

SRNL Legal Signature

Signature

Date

Hyperspectral Raman Imaging using a Spatial Heterodyne Spectrometer (SHS)

Project Team: Alicia Fessler (Primary), Willis Jones, Robert Lascola, and Patrick O'Rourke

Subcontractor: Michael Angel (USC)

Project Type: Standard

Project Start Date: October 1, 2018
Project End Date: September 30, 2020

SRNL, and the larger community, has limited chemical-specific imaging (CHI) capabilities, which would be beneficial for remote detection of threat chemicals or use in inaccessible/harsh environments, as well as in-line process monitoring. CHI is underdeveloped due to issues of sensitivity, stable alignment and calibration, and ease of operation associated with most optical instruments. The project objective is to develop a novel, rugged, highly sensitive spectrometer to support real-time, CHI using hyperspectral Raman spectroscopy. Raman spectroscopic analysis will provide chemical specificity and using a spatial heterodyne spectrometer (SHS) will increase the sensitivity due to the high light throughput design. The instrument will be assembled and initially applied to Raman gas detection of the Saltstone disposal unit headspace gas concentrations. Raman gas analysis is the most impacted by sensitivity issues and will be used to demonstrate the increased light collection capability of the SHS over a conventional dispersive spectrometer.

FY2020 Objectives

- **Set up Holospec f/1.8 spectrometer and run comparison study using H_2 to determine the improved sensitivity for Raman measurements using the SHS.**
- **Demonstrate hyperspectral imaging of relevant samples and develop data analysis/processing algorithms.**
- **Laser stability testing on a UAV to improve understanding of capabilities for using rovers/UAVs for deploying spectroscopic instrumentation.**

Introduction

The Spatial Heterodyne Spectrometer (SHS) is a recently developed technology for optical spectroscopy that promises enhanced sensitivity and new opportunities for process and field measurements compared to conventional spectrometers. Sensitivity gains of 10-100x are obtained through light collection over a wide field-of-view and measurement across a two-dimensional detector array. The SHS may provide a faster response time to facilitate process controls and reactions to emerging off-normal conditions, as might be used when monitoring dissolver headspaces for flammability concerns. With no moving parts, a SHS can support the use of typically delicate laboratory instrumentation in a field environment. More novel measurement applications take advantage of the 2D nature of the detection for obtaining images of the scene. One dimension can be used to provide spatial information at the sample, permitting chemically sensitive imaging that can provide real-time determination of chemical distributions. Examples where such information would be valuable include imaging chemical concentration gradients in a process vessel and rapid detection of "residues of interest" across a wide area. With sufficient development, temporal information may also be obtained, permitting tracking of rapidly evolving chemical reactions.

Saltstone disposal unit 6 (SDU6) requires controls to ensure the flammable gas concentration limit for a list of chemicals is not exceeded, left image in Fig. 1. Calculated estimates of gas concentrations are very conservative and experimental measurements are needed to provide accurate gas concentrations to fill the tank with the appropriate amount of waste without exceeding the concentration limits. *In-situ* measurements are ideal to provide real-time analysis of the conditions within the tank. However, the current tests require pulling a sample through a sampling loop, right image in Fig. 1, and the sampling loop does not work as intended.

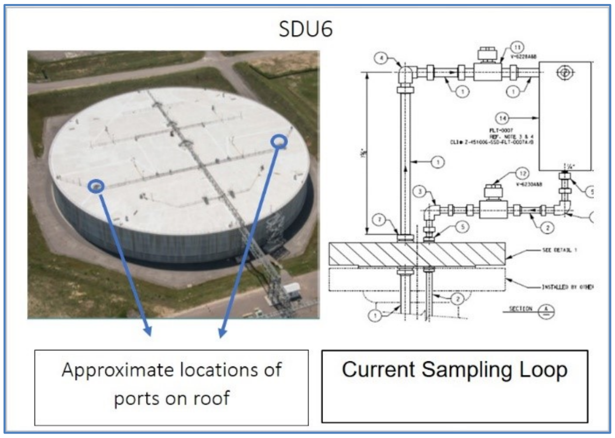

Figure 1: *Saltstone Disposal Unit 6 and Sampling Loop*

Approach

Raman spectroscopy is an optical scattering technique which provides a molecular "fingerprint" of compounds in the solid, liquid, or gas phase. Raman scattering is an inherently weak technique, as only 1 in 10^8 photons are Raman scattered. Increasing the irradiance of the laser, the number of molecules excited, or the collection efficiency are ways to improve signal strength. Of these methods, irradiance is often limited by sample photodegradation, and gases have the lowest molecular density of all sample phases which cannot be improved without pre-concentration. Therefore, increasing collection efficiency is the most viable option but has historically had several challenges. Conventional dispersive spectrometers typically obtain high spectral resolution at the cost of low collection efficiency due to the slit-based spectrometer design. Michelson interferometeric spectrometers offer large collection efficiency, but wavelength separation is achieved via a moving mirror which must travel large distances (ultraviolet) or in an extremely stable environment (mid-infrared) for high resolution. Both conditions provide challenges for operation in a process or field environment.

A new type of interferometric spectrometer, the spatial heterodyne spectrometer (SHS), has recently been adapted for Raman spectroscopic analysis, Fig. 2.[1-6] The instrument offers large collection efficiency and high resolution in a system with no moving parts. With no moving parts, the SHS design promises the ruggedness and stability required for instrumentation being placed in a facility or used in the field. The spectrometer design also allows for monolithic units to be engineered for specific wavelength ranges. As stated above, increasing the collection efficiency is an approach to improve the sensitivity of a Raman measurement technique, and the SHS is a spectrometer that offers large collection efficiencies without compromising resolution or instrument size and stability. We propose to investigate the collection efficiency improvements for gas samples in a backscattering (180°) or perpendicular (90°) sampling arrangement when using an SHS. Depending on the optical set up, we expect to achieve a collection efficiency 10-100 times larger when using a SHS. The corresponding increases in sensitivity would make Raman spectroscopy a more attractive option for gas monitoring applications such as the SDU headspace analysis for flammable species. Sensitivity improvements could be used to lower detection limits, increase the speed of detection and response, or a combination of the two. The first year of the project focused on building an SHS and assembling a gas sample cell measurement scheme. The collection efficiency study, to compare the SHS to a conventional dispersive spectrometer, was delayed due to issues with measuring Raman spectra. Year two began with troubleshooting the instrument and Raman measurement set-up to determine and fix any issues preventing the collection of Raman spectra followed by optimization of instrument and collection parameters, as well as acquiring first Raman gas phase measurements with the SHS.

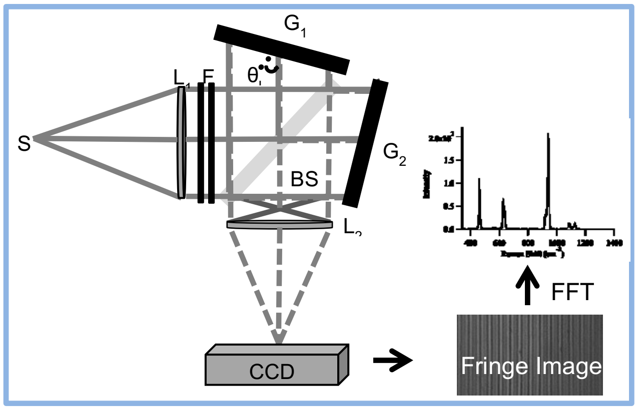

Figure 2. SHRS schematic; fringe image, and Raman spectrum from fast Fourier transform of fringe image.

Results/Discussion

The SHS specifications were designed for the Saltstone off-gassing detection of H_2 and NH_3. The SHS was built to operate in the visible electro-magnetic spectrum using a commercially of the shelf (COTS) laser at 532 nm to take advantage of the increased Raman efficiency at shorter wavelengths. A spectral resolution of 30 cm^{-1} is more than adequate for discriminating the Raman bands of H_2 (540, 655, and 4160 cm^{-1}) and NH_3 (934, 967, 3340, and 3659 cm^{-1}),[7-9] thus 50 gr/mm gratings were used to increase the spectral range to cover the entire Raman fingerprint region 0 - 4200 cm^{-1}. With the new gratings, the rotational and vibrational lines of H_2 and D_2 were measured simultaneously without any spectrometer scanning mechanisms, Fig. 3. The spectra in Figure 3 show H_2 and D_2 are easily discriminated, as well as the rotational lines of H_2 and D_2 are 110 and 45 times more intense, respectively, than the vibrational lines. Therefore, H_2 analysis will use the rotational lines to determine the presence of H_2 off-gassing. The SHS system was used to measure the Raman spectra other common gases (CO_2, N_2, and air) to demonstrate capability to discriminate various gases, Fig. 4.

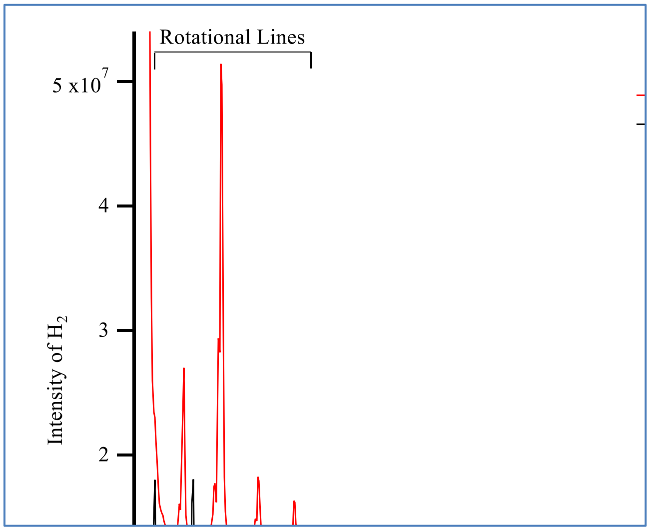

Figure 3. Raman spectra of H_2 (red) and D_2 (black) measured using 1.4 W, 532 nm laser for 10 min. Full spectral range with no moving parts in the spectrometer. Spectra offset for clarity.

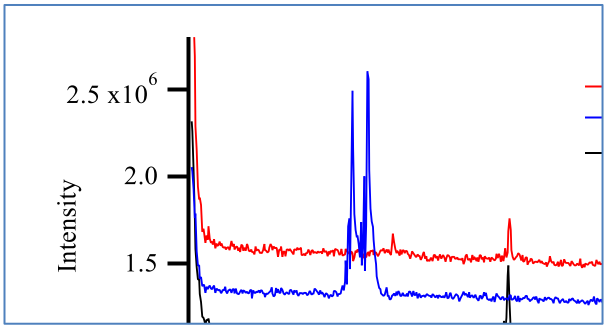

Figure 4. Representative Raman spectra of air (red), CO_2 (blue), and N_2 (black) measured using 1.4 W, 532 nm laser for 10 min. Spectra offset for clarity.

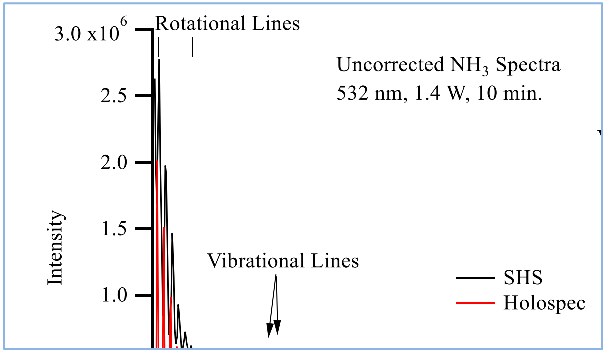

Figure 5. Raman spectra of NH_3 measured using the SHS (black) and Holospec (red) using 1.4 W, 532 nm laser for 10 min. Spectra offset for clarity.

Pure NH_3 and 1% H_2 were measured using the SHS and a Holospec f/1.8 commercial dispersive spectrometer to compare the performance. The uncorrected Raman spectra of NH_3 measured using each instrument are shown in Figure 5. The H_2 data is not shown here. The resolution for the Holospec at the 343 cm^{-1} rotational band was ~6.4 cm^{-1}, while the SHS resolution was 21 cm^{-1}. The result is expected as the grating used in the Holospec is a higher groove density than the SHS gratings. Despite the lower resolution using the SHS, all the spectral features necessary for discrimination and detection are discernable. To make a fair comparison of signal collection, the Holospec NH_3 and H_2 data were corrected for differences in detector settings and quantum efficiencies. The SHS exhibited 7-8 times higher signal than the Holospec for each analyte. Due to differences in noise distribution, only an estimate of the signal-to-noise ratios (SNR) were calculated and showed the Holospec SNR was 3 times better than the SHS. However, the Holospec data was riddled with hot pixels and gamma rays as can be seen when comparing the flat areas of spectrum in the SHS data to Holospec data. The 1% H_2 Holospec spectrum was difficult to discern amid the hot pixels and gamma rays and required background correction to see the Raman peaks clearly. The comparison between the two spectrometers shows the SHS collects more light at sufficient SNR in a compact system capable of easier field deployment.

To determine if the SHS could be used on an unmanned aerial vehicle (UAV) for field analysis such as plume detection, a laser was attached to a Typhoon UAV and the pointing stability was measured 9 m from a target, Fig. 6. Laser pointing stability is important when using spectroscopic systems, because the illuminated sample signal must reach the spectrometer for analysis. Consequently, if the laser cannot be held in a defined area, then the signal will be lost. Given the large etendue of the SHS, the system can measure the signal over an approximately 480 mm diameter at 9 m. The laser pointing stability test demonstrated the Typhoon UAV could hold the laser within a 76 mm diameter, which is 6 times smaller than the SHS viewing limits. Recently a monolithic SHS was demonstrated for Raman spectroscopy by the Angel group at USC, and the SHS weighed 80 g.[7] A high-quality lens, low-noise spectroscopy camera, and other necessary parts for collecting the Raman-scattered light along with the SHS would weight ~3 kg. Commercial UAVs payloads range from 4 g to 220 kg.[8] Therefore, the SHS could be used with a commercial UAV with the proper weight payload capacity.

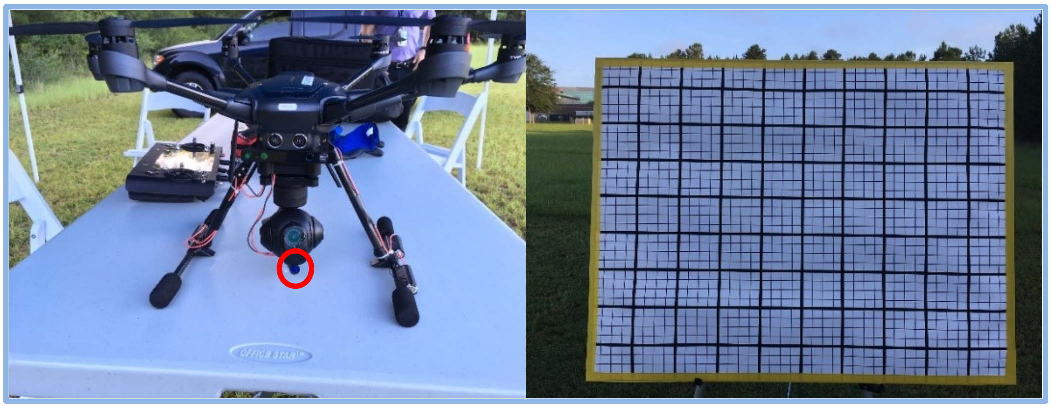

Figure 6. UAV laser pointing stability test drone (left) and target (right). The laser (circled in red) was attached to the drone camera, and the camera recorded the laser spot on the target.

FY2020 Accomplishments

- SHS was demonstrated to measure down to 1% H_2 and should be able to measure 5 times less NH_3. The flammability limit is 4%, so the SHS can detect the H_2 concentration before the limit is reached.
- The SHS collected 7-8 times more light than a commercial dispersive system with an SNR 3 times lower.
- A laser pointing stability test on a UAV was performed to determine if the UAV was stable enough to allow for aerial measurements using the SHS. The large etendue of the SHS provides a viewable diameter ~6 times that of the pointing stability of the laser. The lightweight payload of the spectroscopic system is compatible with the weight limits of commercial UAVs.

Future Directions

- Writing publication with collected data.
- Exploring external funding sources.

FY 2020 Peer-reviewed/Non-peer reviewed Publications

Fessler, K. Alicia Strange; Waldron, Abigail; Colon, Arelis; Carter, Chance; Angel, Stanley. “A Demonstration of Spatial Heterodyne Spectrometers for Remote LIBS, Raman, Spectroscopy, and 1D Imaging.” Spectrochimica Acta B. Invited paper. Submitted 09/14/2020.

Presentations

NA

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Acronyms

CHI	Chemical-Specific Imaging
SDU	Saltstone Disposal Unit
SHS	Spatial Heterodyne Spectrometer
SNR	Signal-to-Noise Ratio
SRNL	Savannah River National Laboratory
UAV	Unmanned Aerial Vehicle
USC	University of South Carolina

Intellectual Property

SRS-19-008: *Static Electric Field Detection Using Raman Spectroscopy to Measure the Depolarization Ratio of Gas Molecules Influenced by Dielectrophoretic Forces*

SRS-19-011: *Detector Mount of Plane Arrays in Optical Spectroscopic Measurement Systems*

Total Number of Post-Doctoral Researchers

Willis Jones is an SRNL post-doctoral researcher who contributed to this work in FY20 by performing work onsite.

Total Number of Student Researchers

NA

External Collaborators (Universities, etc.)

Michael Angel (USC)