Contract No:

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Disclaimer:

Hyperspectral Raman Imaging using a Spatial Heterodyne Spectrometer (SHS)

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. Chemical imaging technology would support multiple directorates through stand-off detection of chemicals (National Security), and imaging of chemical distributions in a process (Nuclear Materials Management, Clean Energy) and in waste tanks (Environmental Stewardship). Chemical-specific imaging 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, chemically specific imaging 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 SHS design does not require moving parts allowing for a very stable system, reducing alignment and calibration issues. 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. The system will be later modified to image spectral information in a spatial domain to provide information on the spatial distribution of a sample scene.

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 publically published in its current form.

SRNL Legal Signature

Signature **Date**

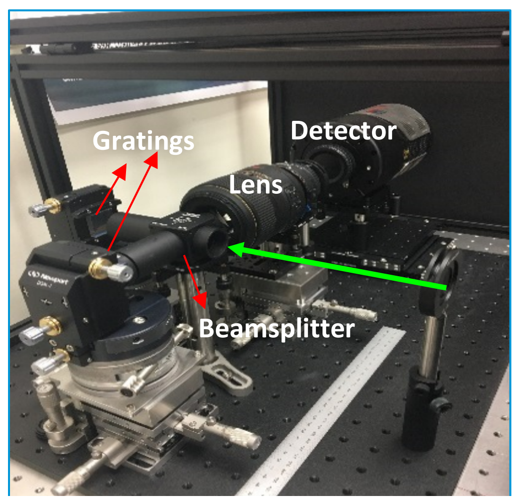

Figure 1: Image of SHRS built at SRNL. Green arrow indicates incoming light.

LDRD-2018-00098
LDRD Report

Hyperspectral Raman Imaging using a Spatial Heterodyne Spectrometer (SHS)

SRNL-STI-2018-00547

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Subcontractor: S.M. Angel (University of South Carolina)

Thrust Area: Environmental Stewardship

Project Start Date: October 1, 2018
Project End Date: September 30, 2019

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 SHS design does not require moving parts allowing for a very stable system, reducing alignment and calibration issues. 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. The system will be later modified to image spectral information in a spatial domain to provide information on the spatial distribution of a sample scene.

FY2018 Objectives

- **Objective 1: Instrumentation assembly and demonstration for Raman gas analysis**
  - Determine and procure (as necessary) components needed to analyze Saltstone-relevant compounds (H_2, NH_3).
  - Design and build a gas sample cell (Fig. 3).
  - Demonstrate ability to measure gas samples with a SHS and compare results to a conventional Raman spectrometer.

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. 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 and the sampling loop does not work as intended.

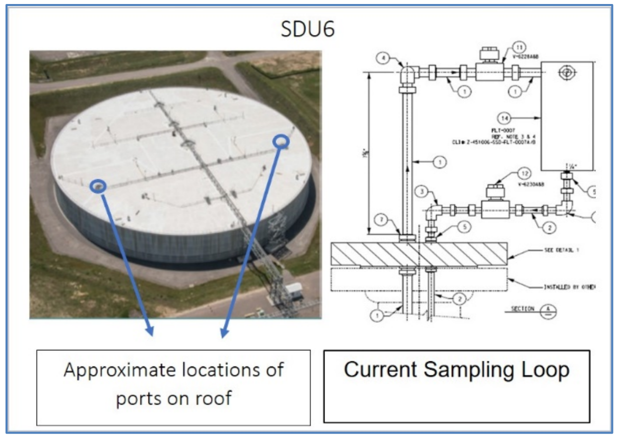

Figure 1: *Saltstone Disposal Unit 6 and Sampling Loop*

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 with only 1 in 10^8 photons Raman scattered, and increasing the irradiance, 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. Increasing collection efficiency has historically had several challenges. Conventional dispersive spectrometers typically exchange spectral resolution for higher collection efficiency due to the slit-based spectrometer design. Michelson interferometeric spectrometers offer large collection efficiency, yet 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.

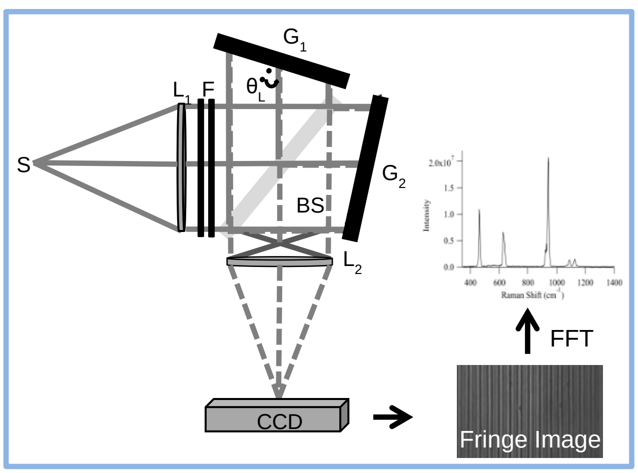

Figure 2. SHRS schematic; fringe image, and Raman spectrum from fast Fourier transform of fringe image.

A new type of interferometric spectrometer, the spatial heterodyne spectrometer (SHS), has recently been adapted for Raman spectroscopic analysis.[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 will focus on building an SHS, designing and assembling a gas sample cell, and measuring the collection efficiency of the SHS in comparison to a conventional dispersive spectrometer. The majority of the first year budget will be dedicated to purchasing the necessary materials to build the SHS, and the remainder will go towards labor for assembling the system and performing the experiments.

Results/Discussion

The SHS specifications were determined based on the SDU application. The flammable gases of concern for the Saltstone off-gassing are H_2 and NH_3. With no known fluorescent compounds present in the samples, the laser wavelength was chosen to be in the visible where commercially of the shelf (COTS) small, powerful lasers and high-quality optics are available and Raman efficiency is better than at longer wavelengths. A spectral resolution of 10 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] Gratings with a groove density of 150 mm gr/mm gratings will produce a resolution of ~2.5 cm^{-1} with a spectral range of ~2200 cm^{-1}. A larger spectral range and less resolution would be more ideal in the future to observe all Raman bands listed using gratings with a lower groove density, but the current arrangement will work well for discriminating the compounds using the Raman bands in the spectral region where both species show a signal. The system components have been procured, received, and assembled (Fig.3).

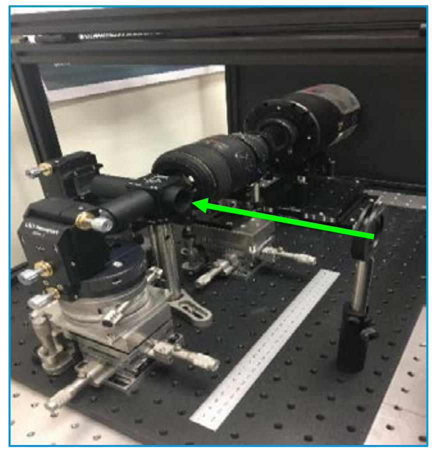

Figure 3: Image of SHRS built at SRNL. Green arrow indicates incoming light.

In the process of assembling and aligning the spectrometer, the spectrum of the emission from a mercury (Hg) lamp was measured. The spectrum to the right is a representative emission spectrum of Hg measured with the SHS constructed at SRNL (Fig. 4). The inset in Fig. 4 shows artifacts on the left side of the 546 nm band. The band artifacts have been determined to be a product of data processing and highlights the importance of developing data processing techniques to produce high-quality data (FY19).

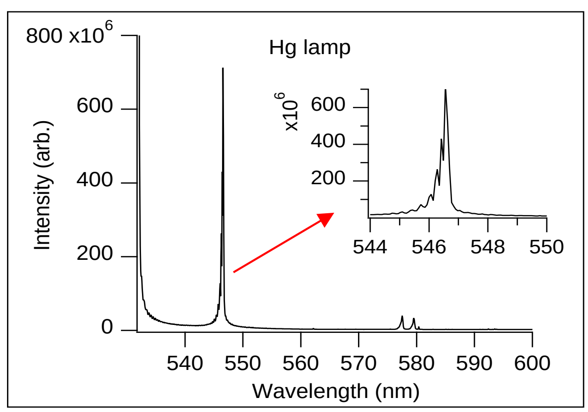

Figure 4: Hg lamp source used for optical alignment and system characterization. Inset shows data processing artifacts.

FY2018 Accomplishments

- Purchased and received all major instrument components and assembled the instrument (Fig.3). Completing the instrument assembly has established the SHS instrument as an optical spectroscopic capability in the SRNL analytical portfolio.

- Identified a focused application for initial demonstration of the SHS. Gas analysis of the headspace above the Saltstone in the SDU6 is the intended application.
- Gas cell assembly was designed and assembled, which provides a sampling system for the Raman gas measurements with the ability to increase the size of the laser beam illuminating the system (Fig.5). The larger beam diameters will allow more analyte molecules to be excited and potentially increase the sensitivity using the SHS to collect and analyze the Raman scattered light, unlike a conventional dispersive spectrometer.

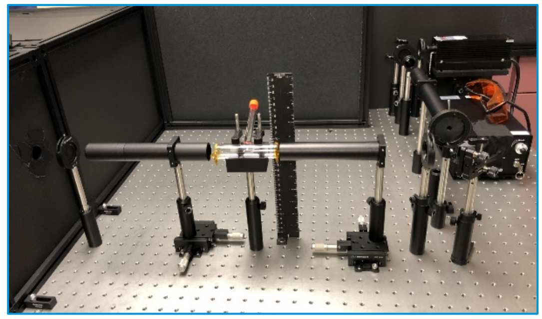

Figure 5: Raman gas sampling assembly.

- Hg measurements were demonstrated using the SHS and are being used to finalize the alignment of the system (Fig.4). The measurements are also being used to begin data analysis procedures.

Future Directions

- **Objective 2: Optimization of SHS system for Saltstone headspace application and demonstrate lab-scale measurements**
    - Lab measurements to demonstrate Raman as a useful technique for Saltstone samples at relevant concentrations (~100s ppm) and to identify potential implementation issues and solutions.
    - Streamlining data acquisition and developing data processing.
- **Objective 3: Adaptation of system for hyperspectral measurements and optimization**
    - Determine the components and arrangement needed to allow for hyperspectral measurements
    - Demonstrate ability to collect hyperspectral Raman images with a SHS

FY 2017 Publications/Presentations

1. Scix Conference oral presentation; October 22, 2018; Atlanta, GA.
2. SERMACS Conference oral presentation; November 1, 2018; Augusta, GA.

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Acronyms

CHI	Chemical-Specific Imaging
Scix	The Great Scientific Exchange
SDU	Saltstone Disposal Unit
SERMACS	Southeastern Regional Meeting for American Chemical Society
SHS	Spatial Heterodyne Spectrometer
SRNL	Savannah River National Laboratory

Intellectual Property

NA

Total Number of Post-Doctoral Researchers

0