

Micro Raman Spectroscopy for Characterizing Molecular Contamination on Space Flight Hardware

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ABSTRACT

In the field of contamination control, many unknowns exist. Often, contamination control engineers have to utilize multiple spectroscopic, macroscopic, and microscopic tools to identify contamination sources when there is a potential contamination exposure to space flight hardware. Understanding the chemical composition of the molecular contamination provides an opportunity for contamination control engineers to determine if this contamination is problematic or benign. In this study, an existing witness plate program for monitoring space flight hardware during the assembly, integration, and testing phases is coupled with micro Raman spectroscopy analysis. The main goal of this study is to determine the limitations, reproducibility, and throughput of micro Raman spectroscopy for characterizing molecular contamination. Micro Raman Spectroscopy will be an additional tool used by contamination control engineers to monitor the cleanliness of space flight hardware.

Keywords: Microscope, Raman, Spectroscopy, Space, Contamination

1. INTRODUCTION

Rapid response and deployable instruments can allow a contamination control engineer to mitigate contamination risks through the assembly, integration, and test life cycle phases of space flight hardware. In recent years, the use of Raman spectroscopy for the characterization of organic and inorganic contamination is a potential method for contamination control engineers to use in the field. However, with any new technique, there have been challenges. Challenges for using Raman spectroscopy as a mitigation method for determining contamination on spacecraft include limitations of the identification of compatible substrates, the competing fluorescence with the weak Raman signal, and the potential for damaging the surface of space flight hardware. Utilizing a 785 nm excitation laser portable B&W Tek i-Raman[®] Plus Raman spectrometer coupled with gold witness plates provided the initial research of the potential for Raman spectroscopy to characterize non-volatile residues (NVR). Use of the portable Raman spectrometer reduced challenges related to the identification of compatible substrates, identified limits of detection for common contamination, and provided solutions to mitigate potentially damaging the surface of direct scanned space hardware. However, the ability to detect mixed contaminants common to space flight hardware was not consistent and required a rapid response and deployable solution. Ideally, this deployable solution could pair with the existing witness plate-sampling program. Specifically, the use of reflective surfaces, such as the gold witness plate, presents a new challenge. The challenge is there is a lack of visual indicator when the laser is in direct contact with deposited NVRs. The lack of a visual indicator on the surface of the gold witness plate will decrease the likelihood of characterizing the deposited NVR. Limitations on the ability to detect NVR could influence the ability to mitigate contamination risks to space flight hardware.

The 785 nm excitation laser portable B&W Tek i-Raman[®] Plus Raman spectrometer has an existing microscope attachment allowing for the ability to utilize micro Raman spectroscopy to characterize NVR deposited or outgassed onto a witness plate. To mitigate the inconsistent data collection with the 785 nm excitation laser portable B&W Tek i-Raman[®] Plus Raman spectrometer, several nitrile glove extraction samples were prepared to observe the limits of micro Raman spectroscopy for characterizing common contamination on spacecraft.

1.1 Materials

Procurement of two-inch diameter p-type silicon wafers with vapor-deposited 50 nm thick gold coating from Ted Pella, Inc. served as the gold witness plate for observing the contamination samples. The cleaning of the glassware included the use of High-Performance Liquid Chromatography (HPLC) grade 99.9% isopropyl alcohol, followed by deionized water rinses. Sample coupon preparation required a collection of samples from sterile nitrile examination gloves purchased from Fisher Scientific. Each sample collection was approximately 3.77 square inches for the nitrile samples. Next, there is an extraction of the nitrile sample in a 50 mL high-performance liquid chromatography (HPLC) grade 99.9% isopropanol solution for 14 days. A commercially purchased acetaminophen standard provided an external calibration source for the 785 nm excitation laser portable B&W Tek i-Raman[®] Plus Raman spectrometer. Shown below in Figure 1 is a picture of the experimental setup of the micro Raman spectroscopy with a 50X microscopic objective and the 785 nm excitation laser portable B&W Tek i-Raman[®] Plus Raman spectrometer.

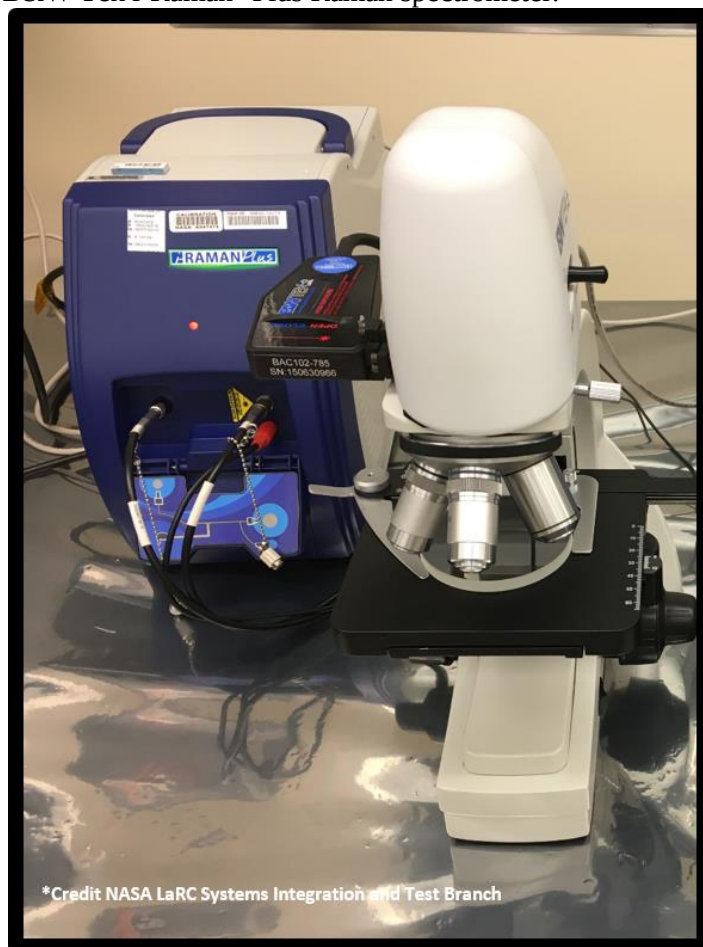


Figure 1: Micro Raman Spectrometer

2. CHARACTERIZATION OF GOLD WITNESS PLATE

Understanding the baseline characterization of the gold witness plate with the 785 nm excitation laser portable B&W Tek i-Raman® Plus Raman spectrometer provided observations of the obstacles preventing the consistent characterization of common spacecraft contamination. Prior research studies with the 785 nm excitation laser portable B&W Tek i-Raman® Plus Raman spectrometer observed detection limits of a phthalate standard at 400 ng per 0.1L² deposited onto a gold witness plate.[1] The concentration of 400 ng per 0.1L² corresponds to an NVR contamination level of AA3.3 per Institute of Environmental Sciences and Technology(IEST)-STD-CC1246E.[1][2]

Deployment of the 785 nm excitation laser portable B&W Tek i-Raman® Plus Raman spectrometer with a gold witness plate as seen in Figure 2, the analyst would have to identify the NVR residue with a visual inspection of the surface with unassisted vision. Known limitations for visual inspections of space flight hardware during ground processing is at a sensitivity of NVR films with a thickness of approximately 5 µm.[3]

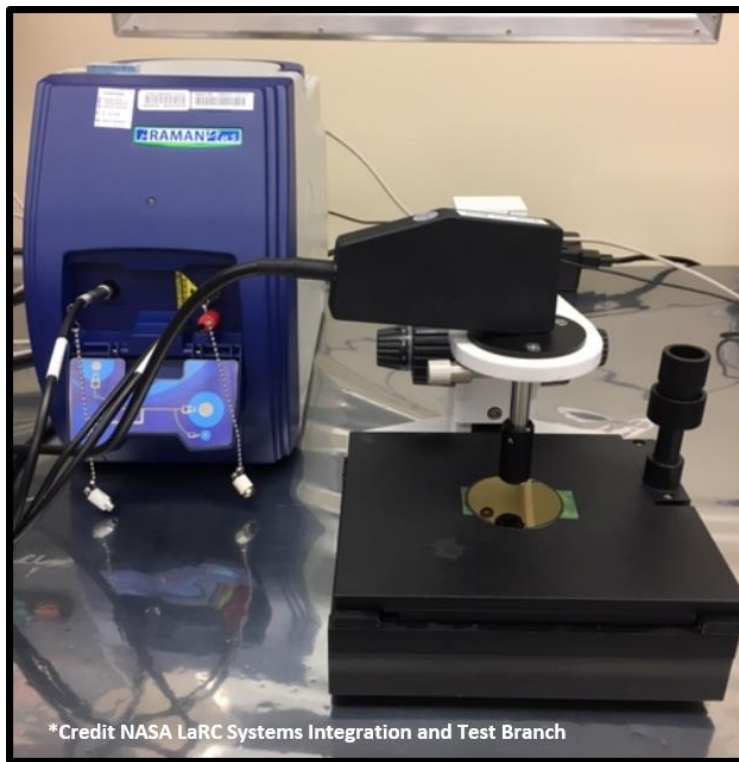


Figure 2: Raman Spectroscopy Characterization of Gold Witness Plate

The use of the 785 nm excitation laser portable B&W Tek i-Raman® Plus Raman spectrometer with unassisted vision limits the detection of NVR deposited onto a witness plate. The 785 nm excitation laser portable B&W Tek i-Raman® Plus Raman spectrometer characterizes the NVR with a power of 340 mW exiting the probe. While characterizing low-level concentrations of NVR deposited on surfaces, there is an increase in the potential of not exciting enough analyte to observe a Raman shift for the specific sample. Further, known phenomena such as sample fluorescence, background fluorescence, and thermal fluctuations from the charged coupled device (CCD) detector can disrupt Raman signal processing.[4] The 785 nm excitation laser portable B&W Tek i-Raman® Plus Raman spectrometer is susceptible to the fluorescence and CCD challenges. These phenomena can overtake

the Raman signal of the contaminant deposited onto the gold witness plate and prevent a complete characterization of the NVR residue.

Shown in Figure 3, an initial characterization of a new gold witness plate provides a baseline with little detectable Raman shifts and relatively low noise. Characterization of a cleaned gold witness plate with the 785 nm excitation laser portable B&W Tek i-Raman[®] Plus Raman spectrometer observed baseline Raman spectrum that observes alkanes, alkenes, ketone, and thiol signatures. The observed Raman bands seen in the spectrum and labeled as A, B, C, D, and E. The observation of cleaned gold witness plates to new gold witness plates observes the Raman spectrum of the new gold witness plate is free from these chemical signatures, respectively. The gold witness plate has a relatively high affinity to the contamination and is the most effective for characterizing NVR in the environment. Cost limitations prevent the ability to use a new gold witness plate for each thermal vacuum (TVAC) test cycle. There is a need for a method that will prolong the use of gold witness plates. In addition, the method will require the use of enhanced imaging capability, the ability to minimize fluorescence, and the detecting of low-level contaminants. Specifically, exploring the microscope accessory for the 785 nm excitation laser portable B&W Tek i-Raman[®] Plus Raman spectrometer could provide a path forward to a cost-effective and enhanced NVR characterization method.

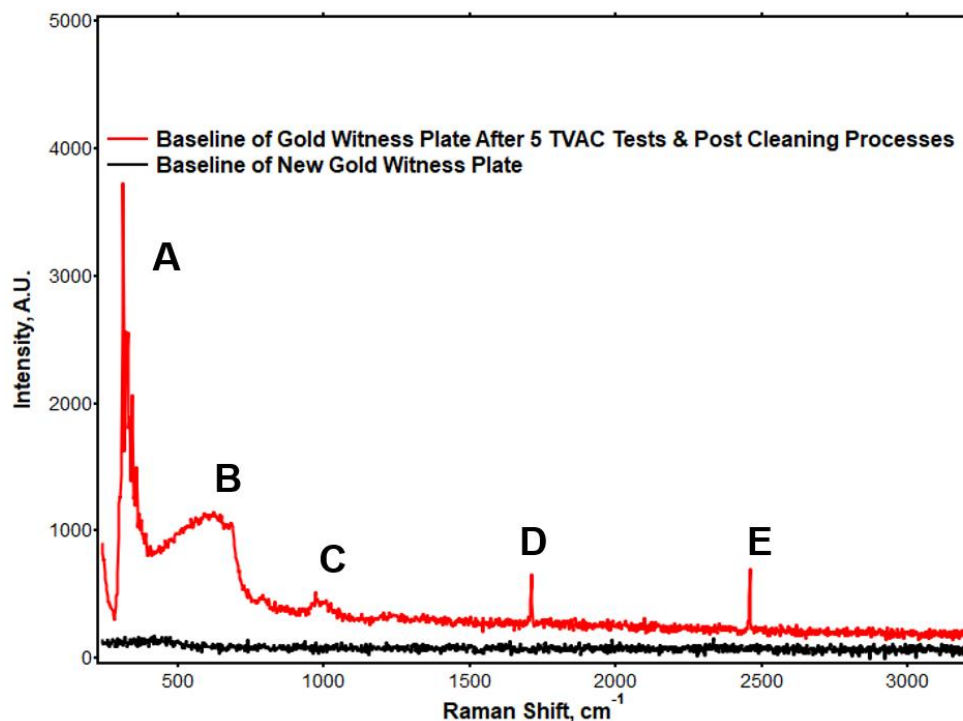


Figure 3: Characterization of Gold Witness Plates with Portable Raman Spectrometer and Laser Probe

3. MICRO RAMAN CHARACTERIZATION OF EXTRACTED GLOVE SAMPLES

An opportunity presented itself to utilize micro Raman spectroscopy to characterize NVR samples. During a routine study of nitrile glove residues, a comparison study of the laser probe accessory and the microscope accessory will provide a proof of concept for enhancing Raman spectroscopy characterization. There is a triplicate analysis of each sample with the 785 nm excitation laser portable B&W Tek i-Raman[®] Plus Raman spectrometer and the specific laser probe and microscope. Next, the deposition of a 100- μ L solution from the

extracted nitrile glove sample onto gold witness plates provides the sample platform. After an overnight drying of each deposited nitrile glove sample, there is a characterization of these samples with the probe accessory and microscope accessory. Characterizing the witness plate utilizing the microscope with the 785 nm excitation laser portable B&W Tek i-Raman[®] Plus Raman spectrometer generates an enhanced image. Seen in Figure 4, the microscopic imaging provides the ability to characterize a sample's microscopic structure, which is a known enhancement of micro Raman spectroscopy. [4]

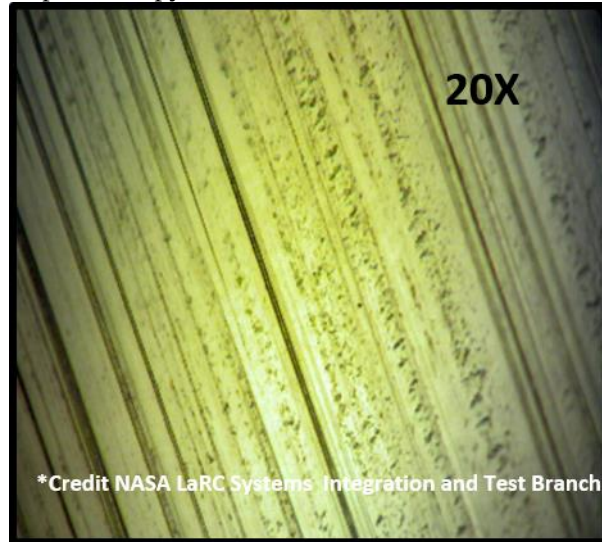


Figure 4: Image of the Gold Witness Plate with the Micro Raman Spectrometer

Characterization of the extracted nitrile glove samples on the gold witness plate with the laser probe accessory and the 785 nm excitation laser portable B&W Tek i-Raman[®] Plus Raman spectrometer provided Raman spectra seen in Figure 5. Raman bands observed from 335 cm^{-1} to 2881 cm^{-1} are common to nitrile-butadiene rubber composites found in nitrile glove material.[5] Further characterization with the microscope accessory and the 785 nm excitation laser portable B&W Tek i-Raman[®] Plus Raman spectrometer is shown in Figure 1 provided an enhanced observation of more distinct Raman bands for nitrile-butadiene rubber composites, respectively. Raman bands observed in the spectrum from the micro Raman analysis of the nitrile glove residue observed more peaks that are significant. Specifically, observation in the spectrum at 1286 cm^{-1} , 1311 cm^{-1} ,

1444 cm^{-1} , 1650 cm^{-1} , 1673 cm^{-1} , 2239 cm^{-1} , and 2488 cm^{-1} in Figure 5 are distinct peaks common to butadiene rubber.[6][7]

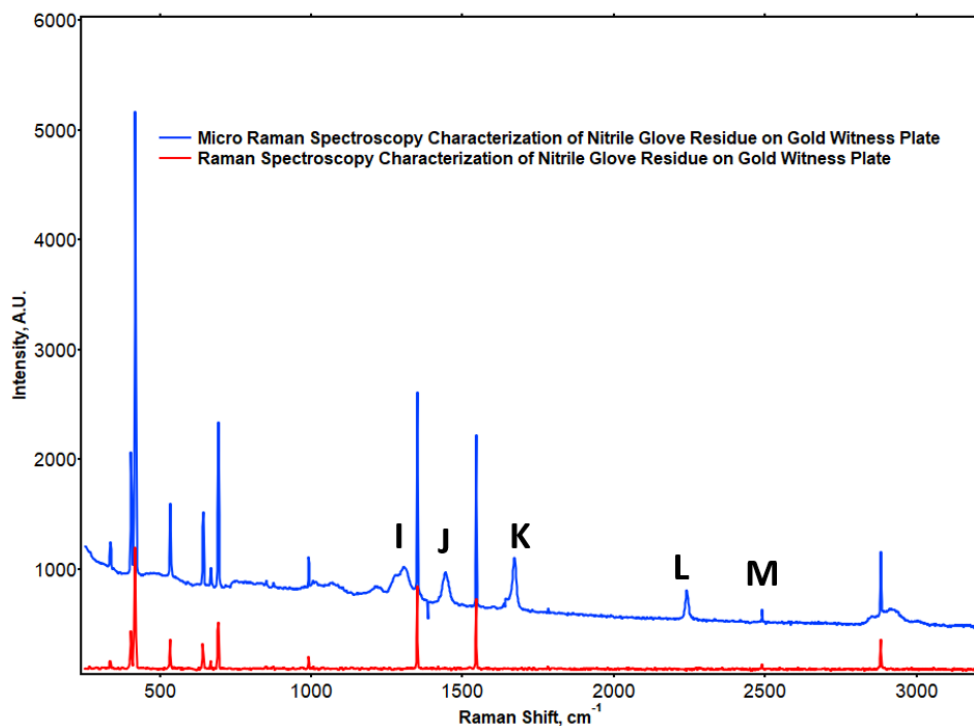


Figure 5: Raman Spectroscopy Characterization of Extracted Glove Residues Deposited onto Gold Witness Plates

The next step is to prepare NVR samples by obtaining 2 mL of the supernatant from the extracted nitrile glove samples to dry onto pre-cleaned aluminum pans. After suspension in chloroform, Attenuated Total Reflectance (ATR) Fourier Transform Infrared (FTIR) characterization will provide validation of observations from the Raman spectroscopic characterization. Shown in Figure 6, the distinguishable IR bands of the nitrile butadiene component common to the nitrile glove residue are present at 1047 cm^{-1} , 1176 cm^{-1} , 1220 cm^{-1} , 1456 cm^{-1} , and 1735 cm^{-1} . [8]

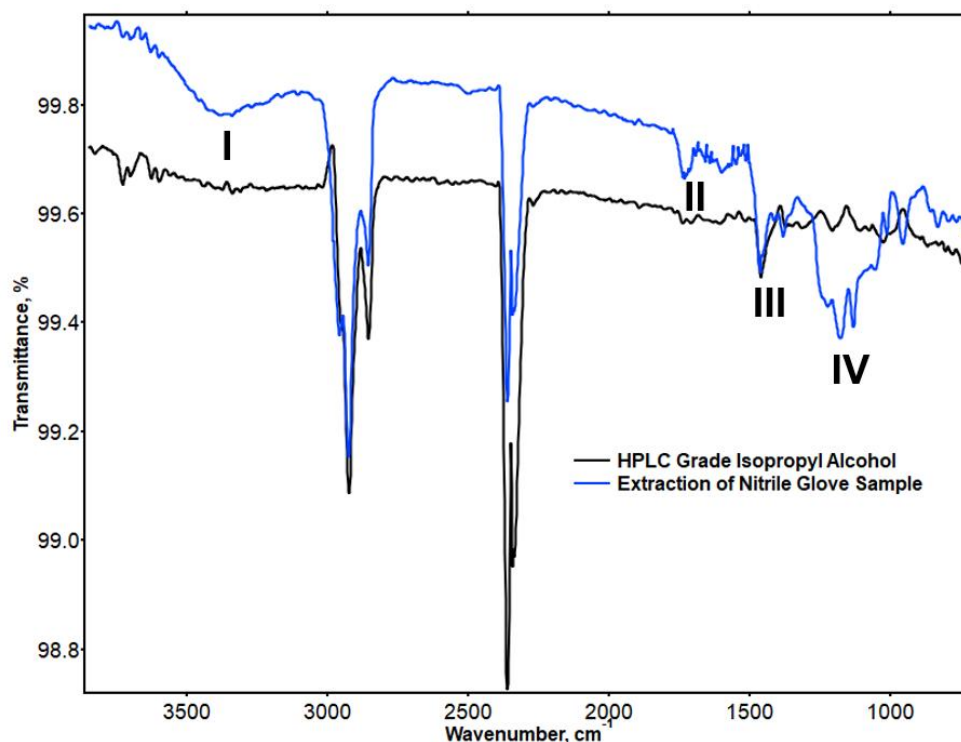


Figure 6: ATR-FTIR Characterization of Nitrile Glove Sample and Isopropyl Alcohol

4. FUTURE WORK AND CONCLUSIONS

Micro Raman spectroscopy is a potential method for determining contamination on space flight hardware. Understanding the limitations of the use of micro Raman spectroscopy will require extensive studies using a wider range of known contaminants to space flight hardware. These studies will include identifying the substrate compatible with this characterization method. The use of gold witness plates as a sampling platform for the NVR and molecular residues with the micro Raman spectrometer provided the ability to observe more Raman shifts specific to an analyte and enhance the likelihood of detection with the microscopic imaging. Future work will focus on applying Raman spectroscopic mapping of the gold witness plates and other surfaces to understand the properties of common space contaminants to understand the potential impact on hardware performance.

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