EXPLORING SURFACE ANALYSIS TECHNIQUES FOR THE DETECTION OF MOLECULAR CONTAMINANTS ON SPACECRAFT

Gugu N. Rutherford, Elaine Seasly, Mark Thornblom
NASA Langley Research Center

James Baughman
Analytical Mechanics Associates, Inc

Abstract

Molecular contamination is a known area of concern for spacecraft. To mitigate this risk, projects involving space flight hardware set requirements in a contamination control plan that establishes an allocation budget for the exposure of non-volatile residues (NVR) onto critical surfaces. The purpose of this work will focus on non-contact surface analysis and in situ monitoring to mitigate molecular contamination on space flight hardware. By using Scanning Electron Microscopy and Energy Dispersive Spectroscopy (SEM-EDS) with Raman Spectroscopy, an unlikely contaminant was identified on space flight hardware. Using traditional and surface analysis methods provided the broader view of the contamination sources allowing for best fit solutions to prevent any future exposure.

Introduction

Contamination control is a mission essential need in the aerospace community. In contamination control various methods are deployed to mitigate risks from particulate and molecular contamination. A presence of particulate and molecular contamination on critical space hardware systems can interfere with system operations leading to performance degradation. Loss in performance can compromise mission goals and create absorbent costs to repair space flight hardware. It is advantageous for contamination control engineers to provide a plan to mitigate contamination risks.

Frequently used methods for mitigating molecular contamination includes collecting swabs, monitoring witness surfaces, collecting rinses, and tape lifts from controlled areas on and near the space flight hardware. Often the analytical methods used to identify the chemical composition of the NVR collected requires analytical test that are performed over a period of days. To mitigate molecular contamination, an area of this research identified the use of SEM-EDS and as a non-contact method to determine the elemental composition of space flight hardware during the assembly phase. SEM-EDS involves the use of a finely focused beam to guide electrons to bombard an area of interest. (ref. 1)The interaction between the electrons from the filament and the sample surface provides characteristic x-rays and images that give information on the morphology, crystallinity, and elemental composition of a sample.

The next investigation involves the use of a hand held Raman spectrometer to provide in situ measurements of space flight hardware during the assembly, integration, and test phase. Raman spectroscopy uses an excitation source of a laser, ranging from 532 nm to 1064 nm, to create a scattering event within molecules known as Raman scattering. (ref. 2) This Raman scattering provides a chemical finger print for every molecule. Traditional Raman spectrometers are pricey bench top units that are limited to a cuvette holder, flow cell, or microscope sample interface. Sample interfaces like cuvette holders, flow cells, and microscopes require small samples and traditional wet bench sample preparation techniques. The expansion of solid state detectors enabled the development of portable Raman spectrometers. Portable Raman spectrometers are advantageous because they are cost effective, portable, and provide unlimited sampling interfaces.

The following case studies will provide data to determine the role of non-contact and in situ monitoring instruments for mitigating molecular contamination on spacecraft. In this investigation a baseline is established for the capability of SEM-EDS and portable Raman spectrometers to assist with contamination monitoring.

Non-contact Methods for Failure Analysis on Space Flight Hardware

During a routine inspection of space flight hardware, there were signs of a visual confirmation of contamination on a radiator panel. As seen is Figure 1, the radiator panel has signs of discoloration. The radiator panel consists of a bulk aluminum surface coated with perforated fluro carbon protected silver tape. In order to investigate the origins of the potential contaminants, wipe and swab samples was collected from the surface of the discolored area. Per the ASTM E1235 – 12, the swab and wipe samples were analyzed to determine the quantity of NVR present. (ref. 3) Next, the swab and wipe samples were extracted and analyzed using FTIR (Fourier Transform Infrared Spectroscopy) and GC-MS (Gas Chromatography and Mass Spectroscopy). FTIR and GC-MS analysis identified only the chemical species common to a negative control wipe and swab. Chemical species common to the radiator panel wasn’t seen in the extracted wipe and swab sample. Without a clear indicator of all the chemical species common to the radiator panel, the identification of the discoloration was incomplete. Further exploration into the identity of the discoloration on the radiator panel would require a surface analysis technique. SEM-EDS was identified as a non-contact method to determine the chemical species on the discolored area of the radiator panel.

The radiator panel was removed from the spacecraft, and placed directly in the chamber of the SEM-EDS. Observations confirmed the chemical identity of the perforated fluro carbon protected silver tape and the bulk aluminum substrate. Shown in Figure 2, are SEM-EDS spectra identifying the aluminum radiator panel, the Inconel layer in the silver fluro carbon protective coated tape, and the remaining species in the perforated fluro carbon protected silver tape.

Next, perforated fluro carbon protected silver tape was removed from the discolored areas of the radiator panel. A microscopic image of the exposed radiator panel is seen in Figure 3. To determine the surface chemistry of the radiator panel, there was a SEM-EDS analysis of the exposed radiator panel. As shown in Figure 4, SEM-EDS spectra confirmed the presence of chloride at 0.5 Wt. % near the points of entry on the perforated fluro carbon protected silver tape.

The amount of 0.5% Wt. % is initially perceived as a small quantity. However, it is important to note that SEM-EDS is on a micron scale. Observations of chloride at the level of 0.5 Wt. % is a relatively high amount for such a small scale. SEM-EDS enables the ability to map an area for chemical composition. To identify the location of the contaminant on the radiator panel, SEM-EDS mapping was performed. In Figure 5, SEM-EDS mapping observed chloride contaminants at the seam of the perforated fluro carbon protected silver tape.

Ideally, a quantitative method would be the preferred method of determining contaminant on space flight hardware. A disadvantage to SEM-EDS is that the method is a qualitative method. (ref. 1) However, the use of a paired technique allows SEM-EDS to provide quantitative analysis of a sample. SEM-WDS, Scanning Electron Microscopy-Wavelength Dispersion Spectroscopy, is a commonly paired instrument with SEM-EDS, and SEM-WDS uses crystal NIST (National Institute of Standards and Technology) standards to identify quantitatively the amount of an element in a sample. (ref. 1) To determine the quantitative Wt. (Weight) % of chloride on the radiator panel, the radiator panel was analyzed with SEM-WDS. As seen in Figure 6, SEM-WDS analysis confirmed areas with chloride as having as much as 44.8 Wt. % near the point of entry on the silver Teflon tape. The vast majority of the data supports the presence of chloride trapped in the points of entry of the perforated fluro carbon protected silver tape. A source for the chloride contamination was identified as a chlorinated solvent.

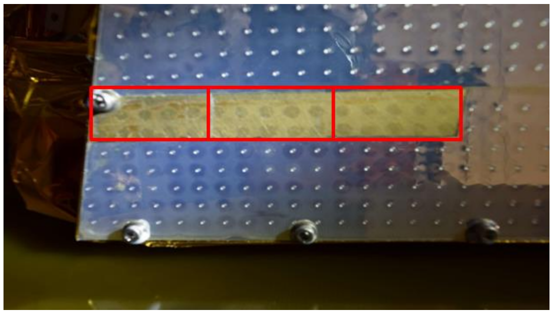

Figure 1: Visual inspection of an aluminum radiator panel with molecular contamination identified under the perforated fluro carbon protected silver tape. (Courtesy of NASA Langley Research Center, 2016)

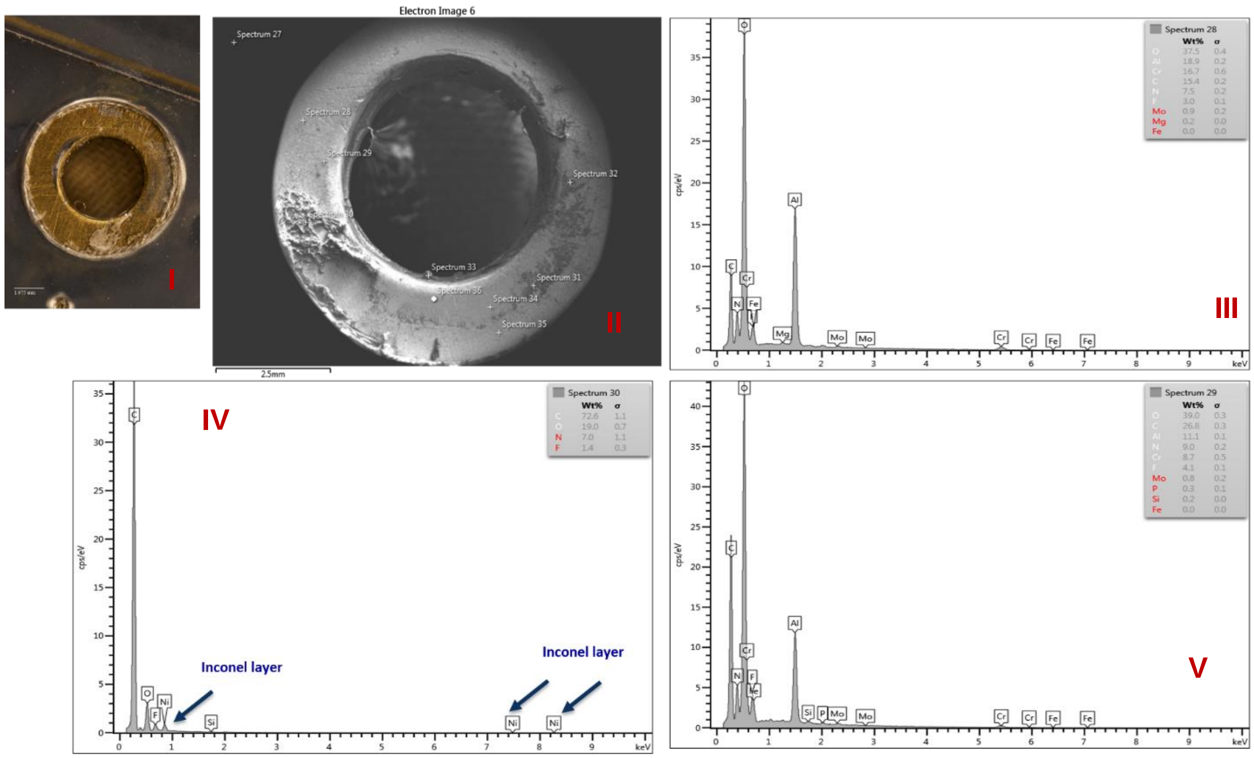

Figure 2: Photographic and microscopic images of the contaminated aluminum radiator panel. (Courtesy of NASA Langley Research Center, 2016) (I,II) Spectra collected from and SEM-EDS scan of the radiator panel. (III, IV, V).

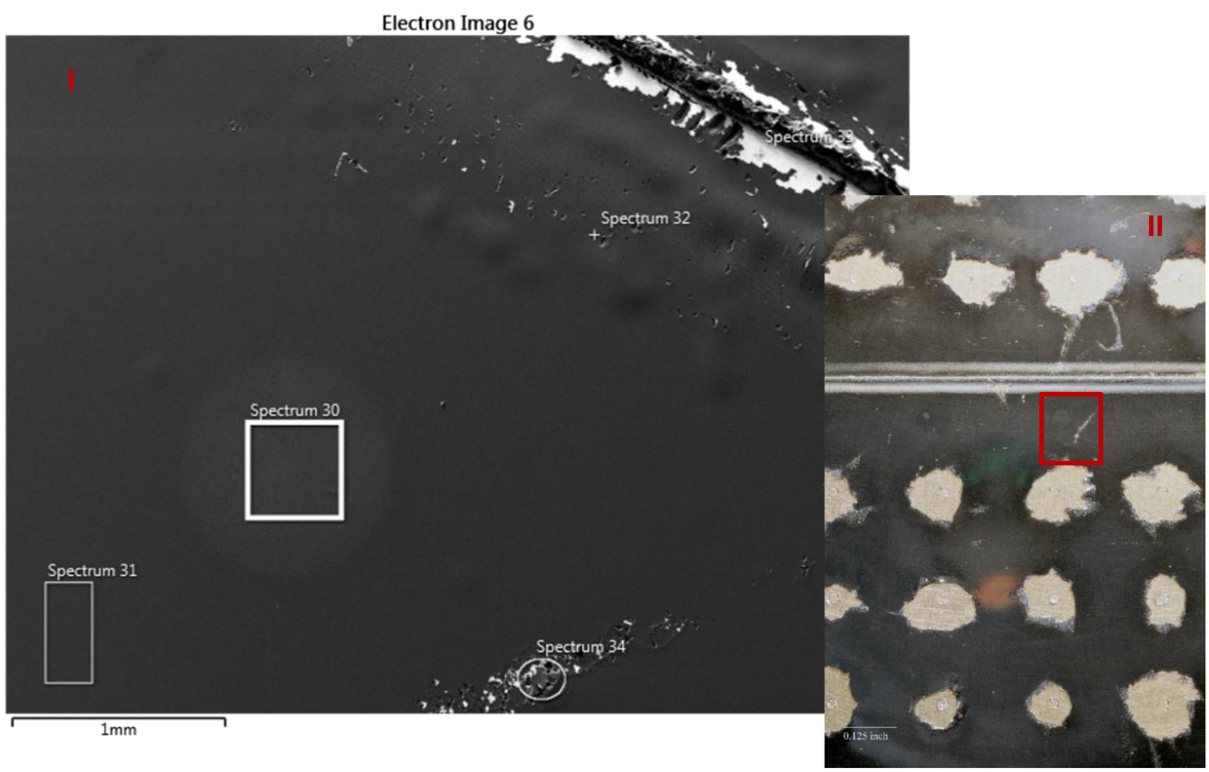

Figure 3: Microscopic image of the radiator panel, and a 'halo' area identified as 'Spectrum 30'. (I) Photographic image of the exact area on the radiator panel, and the identification of the 'halo' are observed in the microscopic image. (Courtesy of NASA Langley Research Center, 2016) (II)

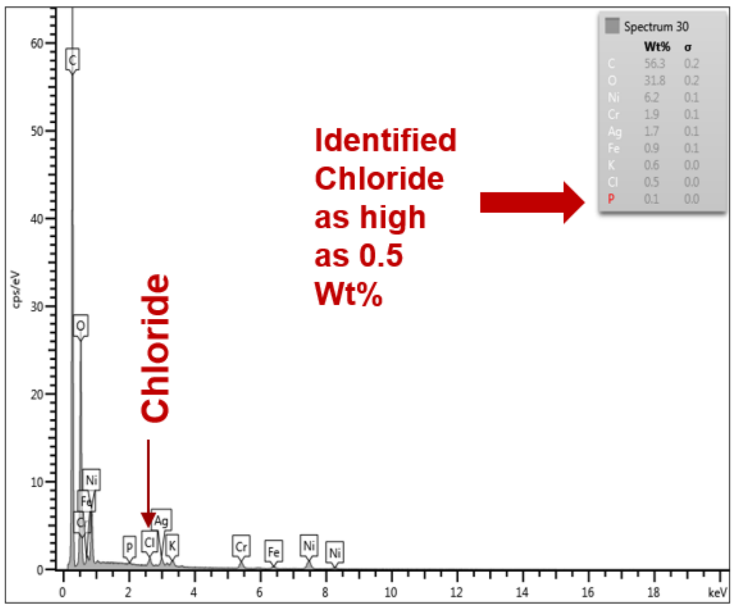

Figure 4: SEM-EDS analysis of the 'halo' area identified in photographic and microscopic images. Spectrum 30 identified 0.5% chloride in the 'halo' area next to the seam of the perforated fluro carbon protected silver tape.

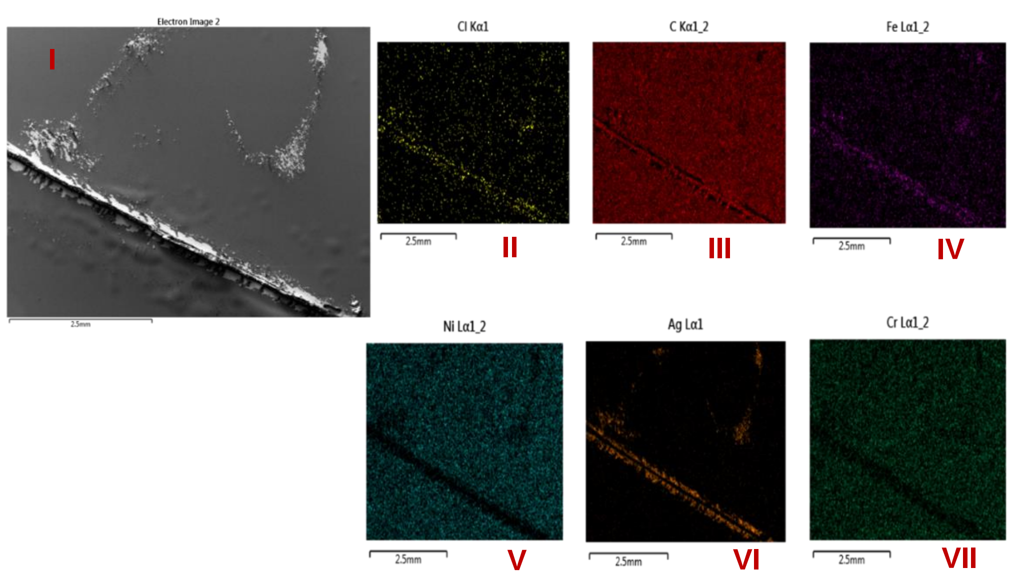

Figure 5: Using the SEM-EDS, a microscopic image of the radiator panel is generated. (I) Mapping of the radiator panel using SEM-EDS indicated chloride in the highest location on the seam of the silver Teflon tape. (II to VII)

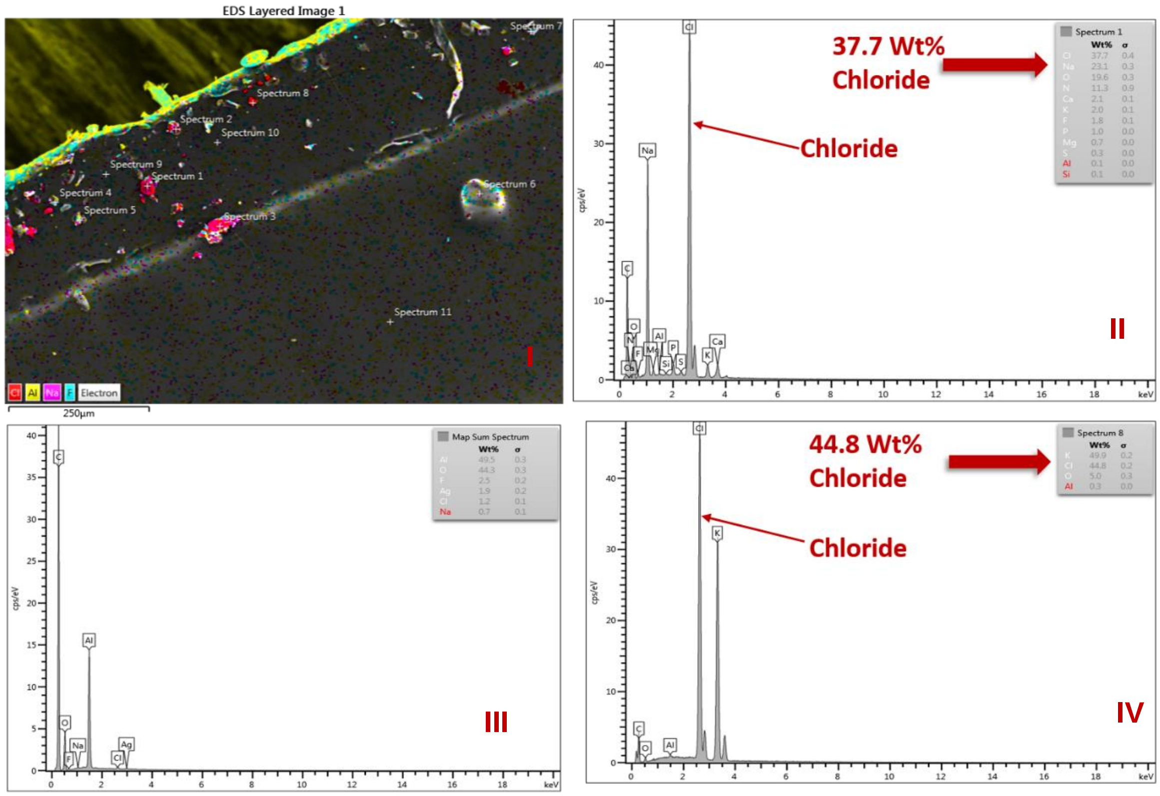

Figure 6: View of a SEM-WDS map of the radiator panel that identifies the location of the chemical elements on the area of interest. (I) Utilizing SEM-WDS to analyze the radiator panel, there was as much as 44.8% chloride quantitatively observed in the points of entry of the silver Teflon tape. (II, III, IV)

In Situ Measurements of Molecular Contamination on Space Flight Hardware

Contamination control is a factor in each phase of the lifecycle for spacecraft. Often, response to adverse effects of contamination occurs later in the lifecycle. The advancement of instrumentation enabled the consideration of new technologies for the mitigation of molecular contamination on spacecraft. Specifically, an analyst can now use a probe to directly access surfaces to obtain molecular composition. To investigate this capability of in situ monitoring of molecular contamination on spacecraft, this research team utilized a portable Raman spectrometer to identify the chemical species of known contaminants deposited onto a coupon. Benefits of the portable Raman spectrometer are that the Raman signal can penetrate transparent materials, the Raman signal has limited matrix interactions from common solvents, and Raman spectroscopy is an in situ measurements on solid, liquid, and gas analytes.

The coupon of interest is a fused silica substrate with 150 nm of aluminum deposited onto the surface. All fused silica substrates where cleaned under ultra-sonication with ACS (American Chemical Society) grade acetone followed by ultra-sonication in ACS grade ethanol. (ref. 4) To prevent cross contamination, these coupons are dried under nitrogen. The aluminum deposition is performed utilizing sputter physical vapor deposition at pressures below 5×10^{-6} Torr. In order to obtain a baseline for the aluminum coated fused silica substrate, a baseline scan is measured using the portable Raman spectrometer. Raman spectrum in Figure 7 identifies a peak at 110 cm^{-1} which corresponds the aluminum oxide species in the coating. (ref. 5)

Polyurethane is a common contaminant to space flight hardware. To identify the potential for identifying polyurethane, a solution of 10% (v/v) solution of polyurethane in ethanol is prepared for Raman analysis. A 10 µl amount of the 10% polyurethane solution is deposited onto the coupon using a micropipette. The solution is allowed to dry under ambient conditions for a period of 24 hours. Next, a series of measurements is performed using the portable Raman spectrometer. The goal is to identify signature peaks of the polyurethane. As seen in Figure 8, the signature vibration modes where identified for the amide band at 1668 cm^{-1}, the stretching of the polyaromatic ring at 1437 cm^{-1}, and the CH_2 twist at 1301 cm^{-1}. (ref. 2) Conformation of the aluminum coating is observed with bending at 112 cm^{-1} for aluminum oxide in Figure 8.

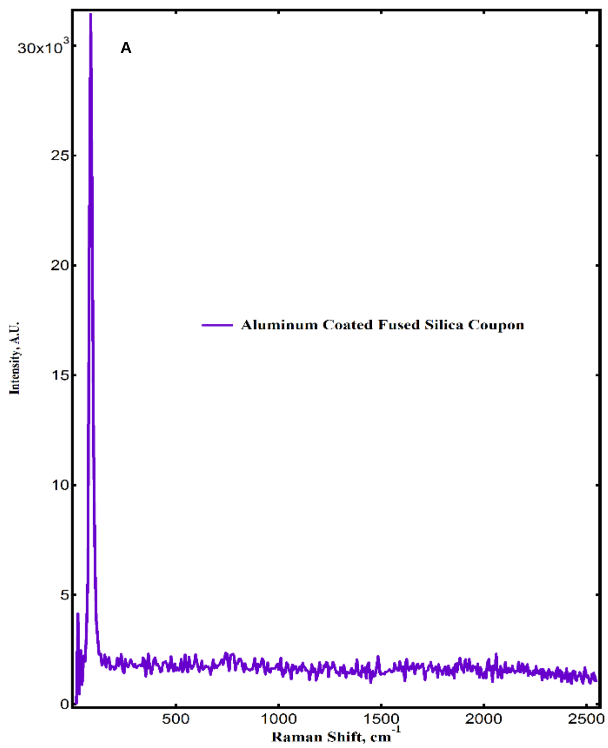

Figure 7: Baseline identification of the aluminum coated fused silica substrate using the portable Raman spectrometer. Observations identified a bend at 110 cm^{-1} for the aluminum oxide in the coating. (A)

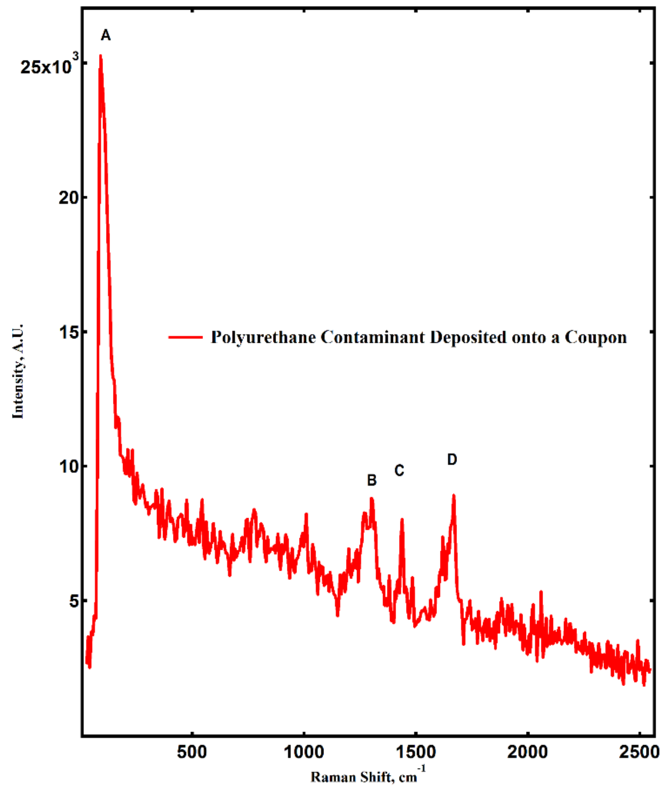

Figure 8: Raman spectrum of a 10% (v/v) polyurethane contaminant deposited onto an aluminum coated fused silica substrate. The aluminum oxide bend is identified at 112 cm^{-1}. (A) A CH_2 twist is seen at 1301 cm^{-1}. (B) Stretching from the polyaromatic ring is observed at 1437 cm^{-1}. (C) Likewise, the amide I band is identified at 1668 cm^{-1}. (D)

Discussion and Conclusion

The use of non-contact instrumentation provides an opportunity to mitigate molecular contamination throughout the lifecycle of the spacecraft. In the case study of utilizing SEM-EDS to determine contamination on radiator panels, the observations confirmed the presence of chlorinated solvents. Early identification of the chloride in the radiator panels ensured the performance of the spacecraft wasn't compromised. Non-contact instrumentation provided a cost and time effective method for protecting the integrity of the mission in the early phases.

In situ monitoring of space flight hardware using a portable Raman spectrometer, provides supportive analysis for determining molecular contamination. By using a Raman spectrometer that can directly interface with surfaces, it provides an initial observation of the surface chemistry of the space flight hardware. Once the chemical species are identified, then findings will provide clues on the next action. An analyst can use the in situ monitoring of space flight hardware with Raman spectroscopy as a screening step to decide if there are potential molecular contaminants that can degrade the performance of a spacecraft. The case study using the portable Raman spectrometer identified the presence of polyurethane on aluminum coated coupons.

Future work will focus on standardizing the in situ monitoring of space flight hardware with Raman spectroscopy. Specifically, the scope of the work will identify a limit of detection for known contaminants and identifying the best parameters for collecting data.

References

1. Goldstein, Joseph I.; Lyman, Charles E; Newbury, Dale E.; Lifshin, Eric; Echlin, Patrick; Sawyer, Linda; Joy, David C; Michael, J. R. *Scanning Electron Microscopy and X-Ray Microanalysis*. (Springer Science + Business Media, 2003).
2. Lambert, Joseph B.; Shurvell, Herbert F.; Lightner, David A.; Cooks, G. R. *Introduction to Organic Spectroscopy*. (Macmillan Publishing Company, 1987).
3. ASTM International. *ASTM E-12345-12_Gravimetric Determination of Nonvolatile Residue (NVR) in Environmentally Controlled Areas for Spacecraft 1*. (2016). doi:10.1520/E1235-12.2
4. Kern, W. & Soc, J. E. The Evolution of Silicon Wafer Cleaning Technology. *J. Electrochem. Soc.* **137,** 1887–1892 (1990).
5. Liptak, B. G. in *Instrument Engineer's Handbook: Process Measurement And Analysis Volume I, Section 8.51- Raman Analyzers* 1609–1610 (CRC Press, 2003).