

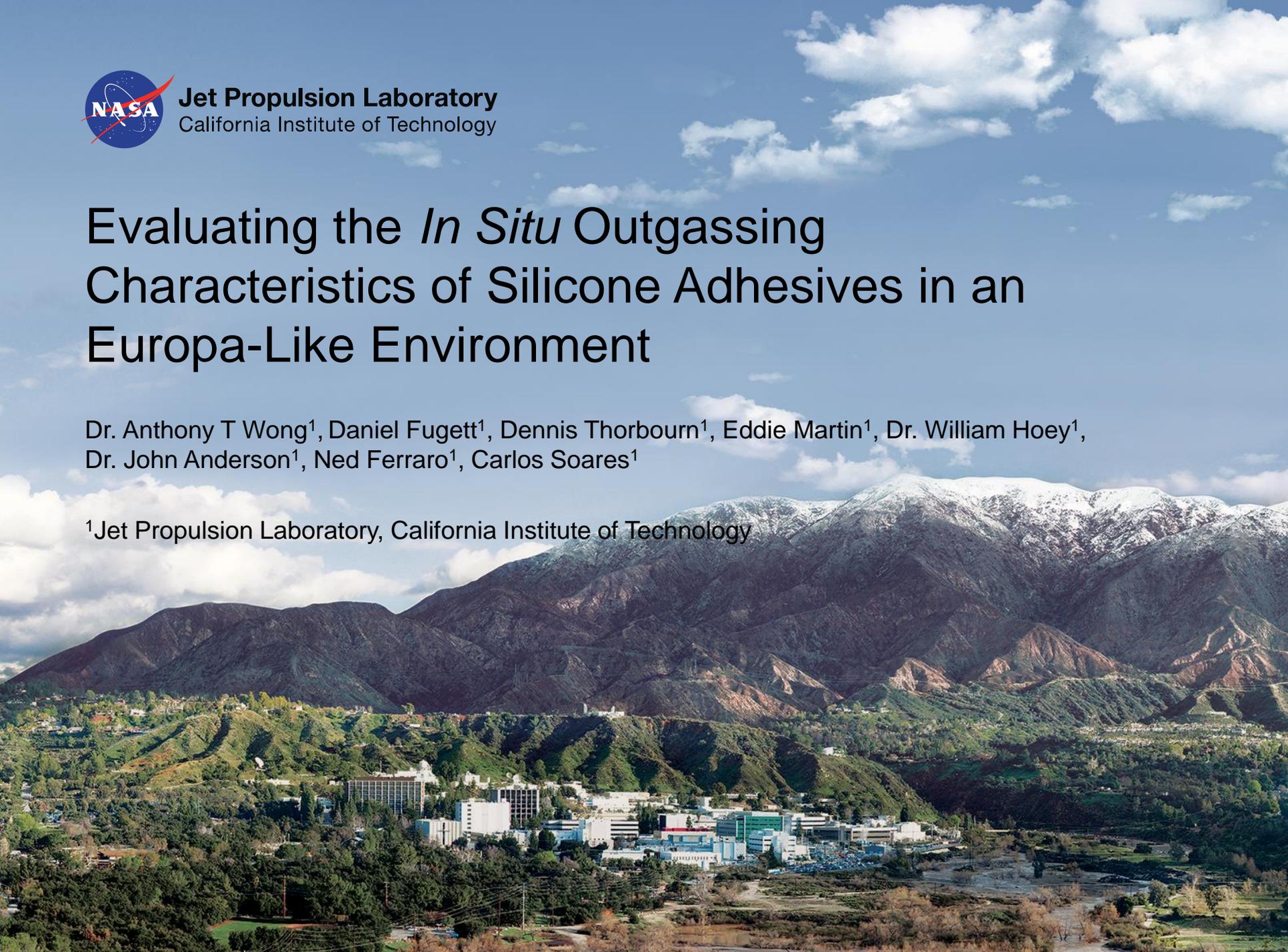


Jet Propulsion Laboratory
California Institute of Technology

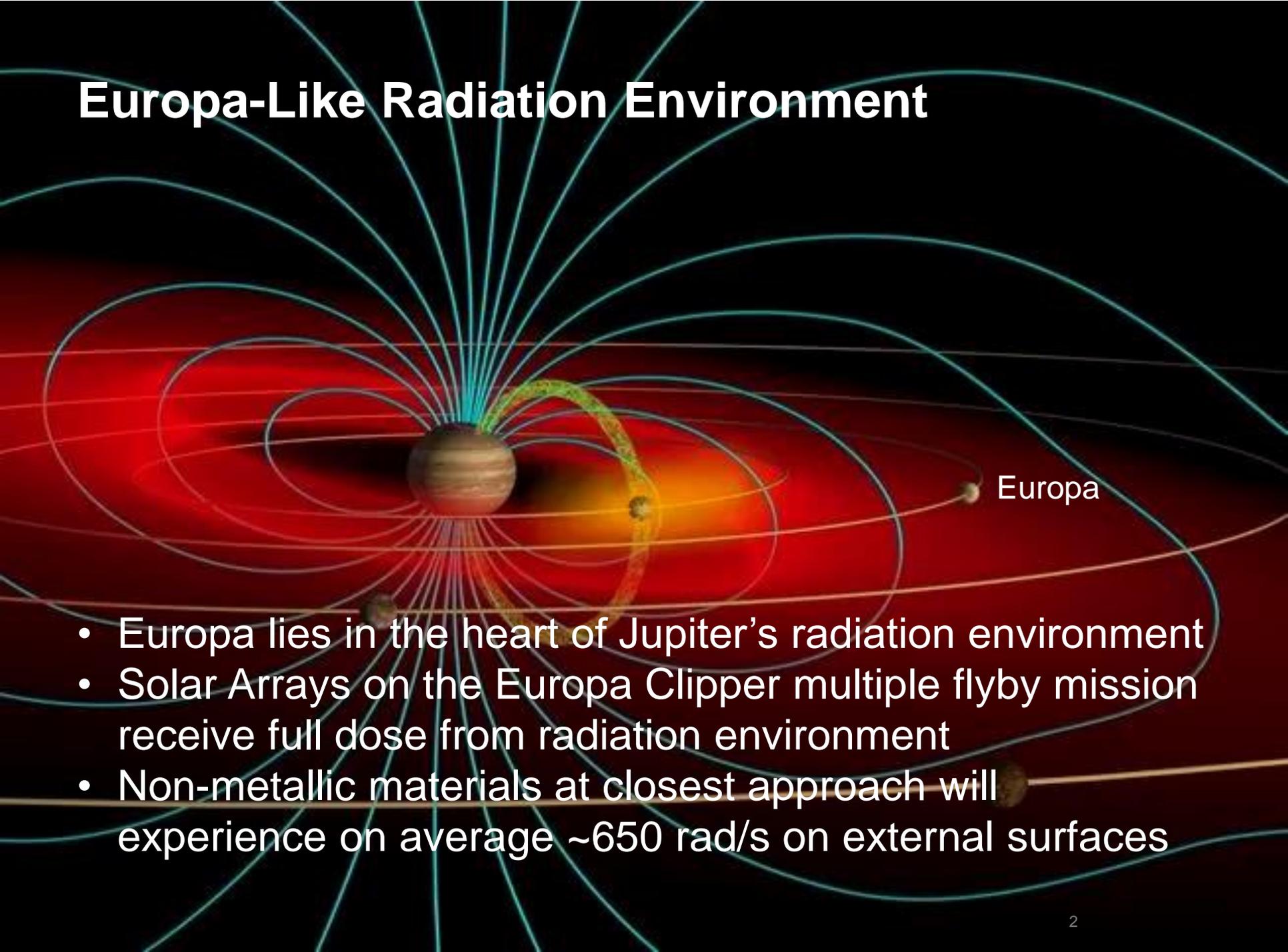
Evaluating the *In Situ* Outgassing Characteristics of Silicone Adhesives in an Europa-Like Environment

Dr. Anthony T Wong¹, Daniel Fugett¹, Dennis Thorbourn¹, Eddie Martin¹, Dr. William Hoey¹,
Dr. John Anderson¹, Ned Ferraro¹, Carlos Soares¹

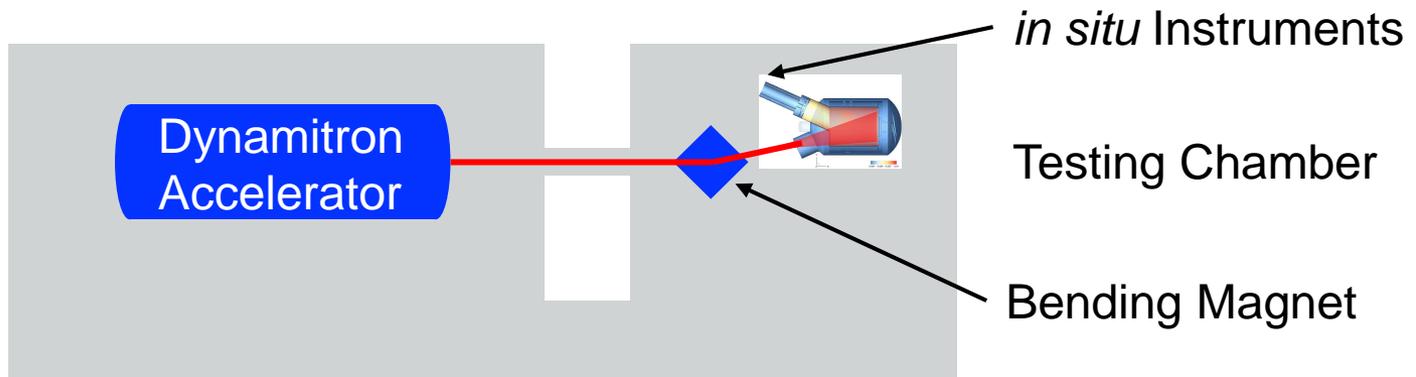
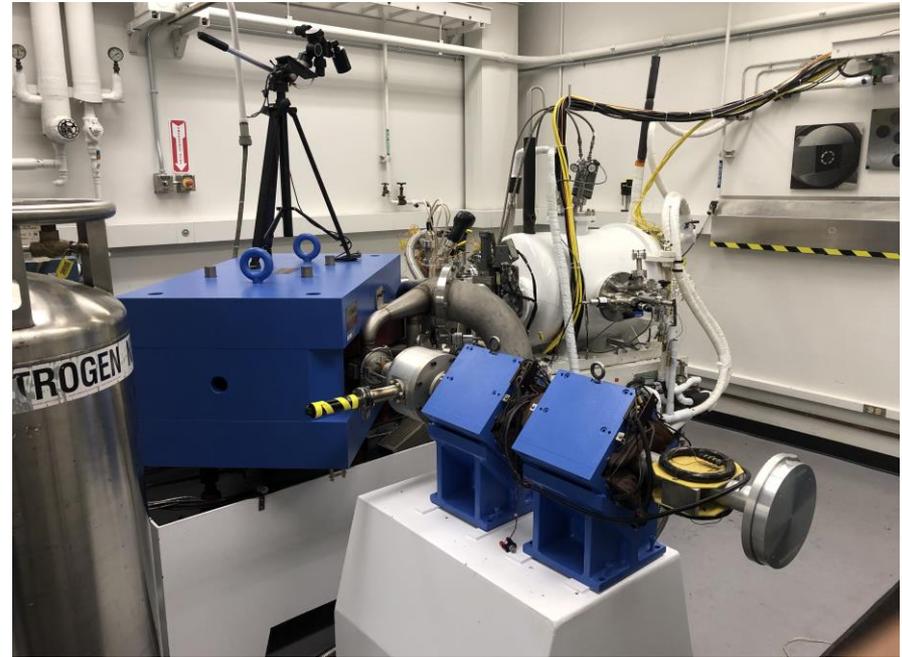
¹Jet Propulsion Laboratory, California Institute of Technology



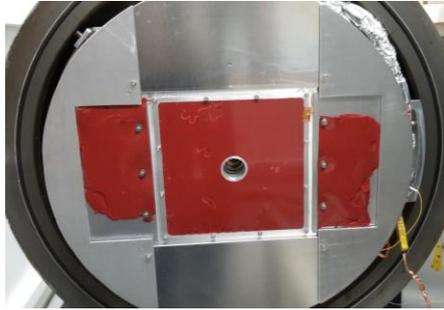
Europa-Like Radiation Environment

- 
- A diagram illustrating the radiation environment around Jupiter. Jupiter is shown at the center, with its characteristic bands. Numerous blue lines represent magnetic field lines extending from the poles. A red, glowing region represents the radiation belts. Europa is shown as a small sphere in the center of these radiation belts. The background is dark with some faint orbital paths.
- Europa lies in the heart of Jupiter's radiation environment
 - Solar Arrays on the Europa Clipper multiple flyby mission receive full dose from radiation environment
 - Non-metallic materials at closest approach will experience on average ~ 650 rad/s on external surfaces

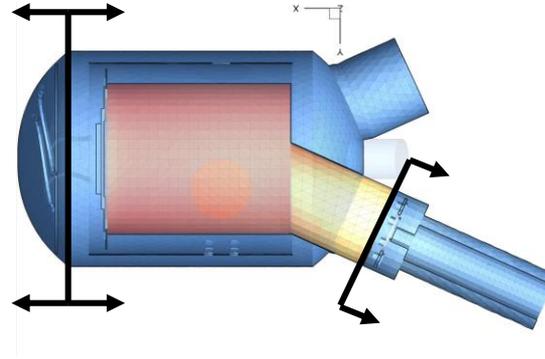
Radiation Induced Outgassing Test (RIOT) Setup



Test Chamber Configuration



Sample Under Test

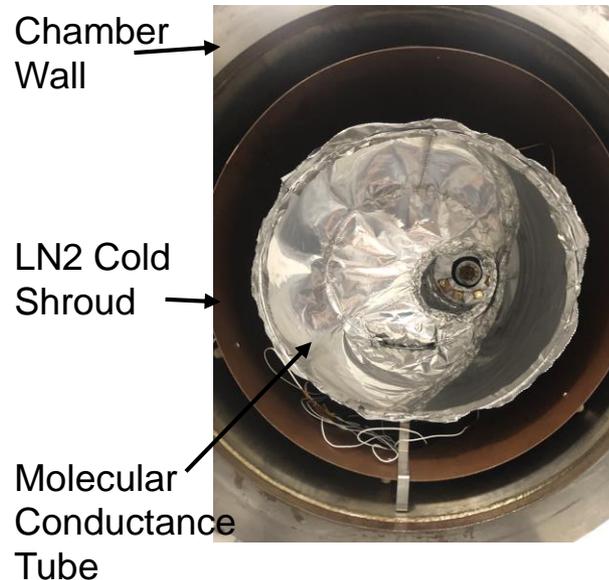


Extrel MAX 1000
Quadrupole Mass
Spectrometer



-133°C -93°C -113°C -173°C
QCM Research MK 18 Cryo
Quartz Crystal Microbalances
(CQCM)

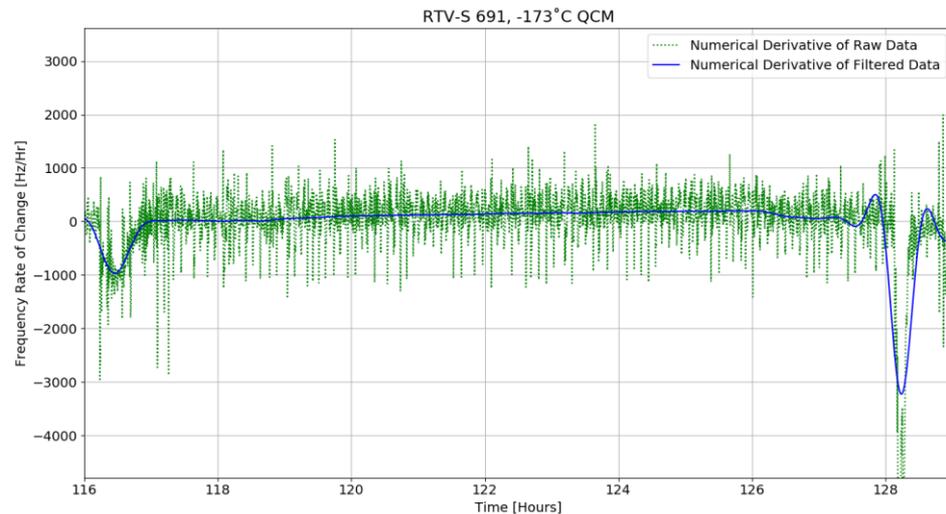
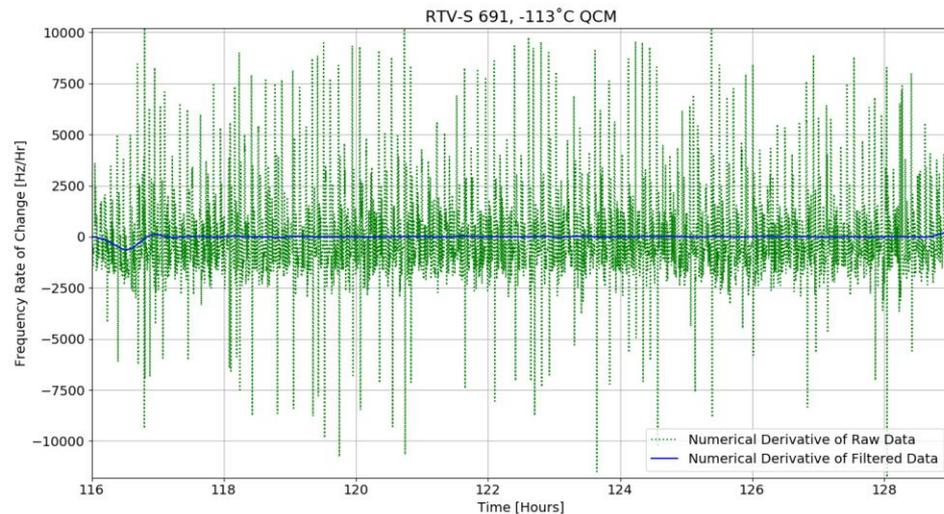
- LN2 Cold Shroud used to get rid of residual vapors in chamber
- Molecular Conductance Tube held at elevated temperature using strip heaters to keep sample outgassing constituents from sticking to cold shroud
- Molecular transport ray tracing model used to calculate the transmission fraction from sample to instruments
(ASEC Presentation on Friday at 8:50 am by Dr. William Hoey)



Testing Parameters and Procedures

- Sample Temperature: $-113 \pm 5^{\circ}\text{C}$
 - Mimics material temperature during Europa flyby
- Electron Energy: 1.5MeV
 - High enough energy to dose samples without imparting charge
- Electron Flux: $2.6\text{E}10 \text{ e-}/\text{cm}^2/\text{s}$
 - Mimics peak flux for average Europa flyby
- Duration: Nominal 8 hour irradiation
 - Maximum time duration for nominal facility operation
 - Average flyby will experience >20 hour irradiation at peak flux

RIOT Instrumentation: CQCMs



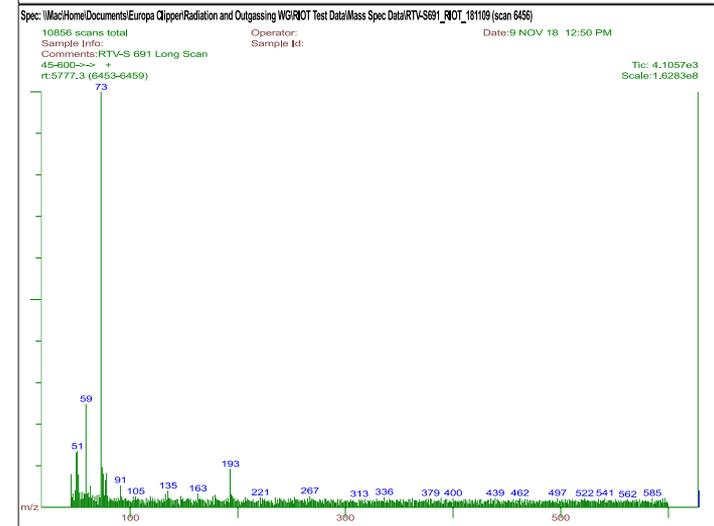
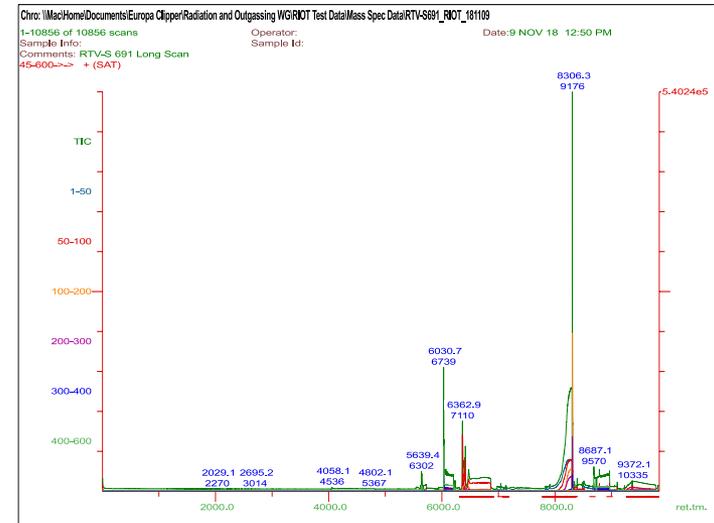
QCM at Temperature

Electron Beam On

- Data are logged through duration of a test run, sometimes as high as 168 hours
- Segments of time are identified as measurement periods
- Raw Frequency Data is often noisy due to limitations in the instrumentation setup
- Low Pass filters are used to reduce signal noise during analysis

RIOT Instrumentation: Mass Spectrometer

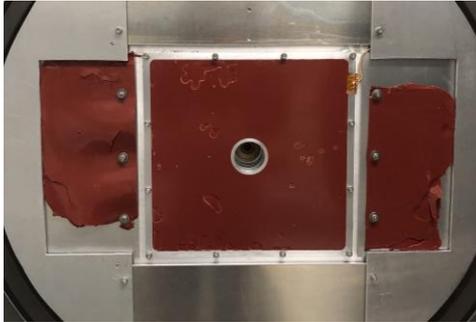
- Extrel MAX 1000 Quadrupole Mass Spectrometer
- Nominal Scan Range m/z of 1-600
- Phase 1 tests collected centroid data
- Phase 2 tests collected spectra data
- Spectrometer pre-amplifier and multiplier settings adjusted during testing to maximize signal to noise for any given test parameter
- Similar to QCMs, data logged continuously through entire test run



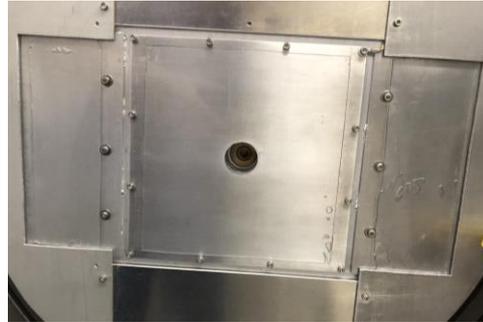
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Merlin Automation Data Systems

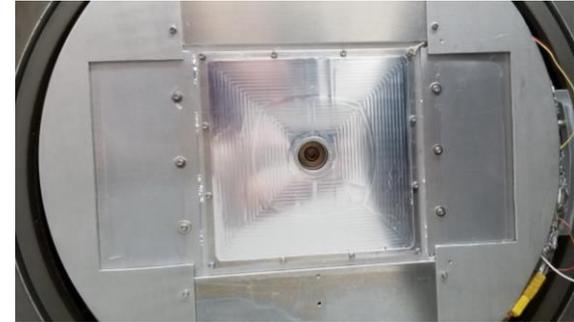
Tested Samples



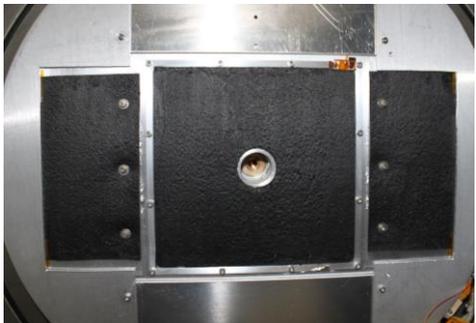
Wacker RTV-S 691



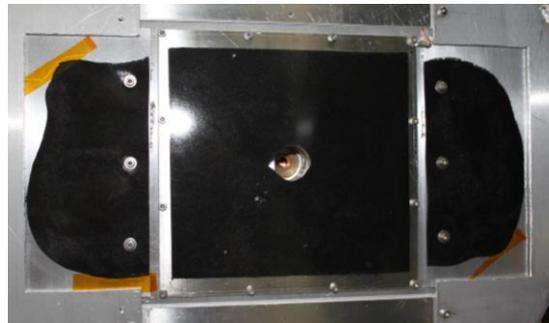
Nusil SCV-2585



Dow Corning 93-500



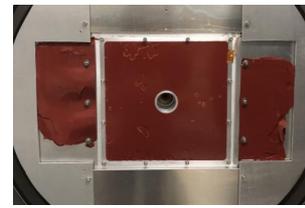
Nusil CV-1500



Nusil SCV-2596

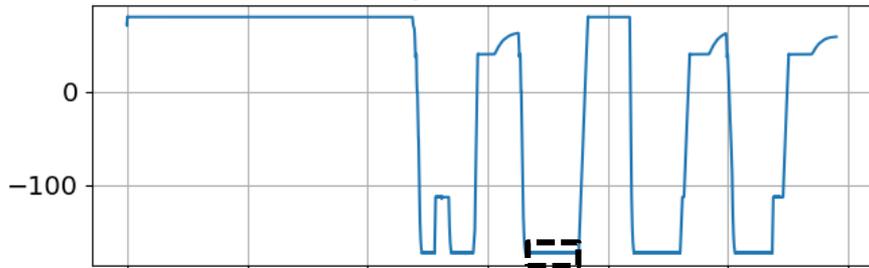
- Silicone materials were mixed and applied per manufacturer specifications
- Cured for 7 days at room temperature
- Baked out at 110°C for 144 hours in $\leq 1E-05$ Torr

Pathfinder Test: RTV-S 691

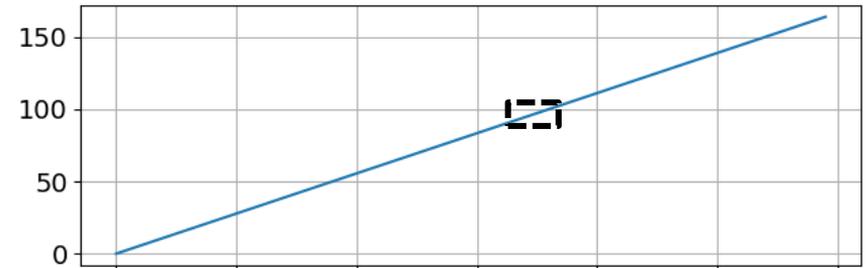


Wacker RTV-S 691

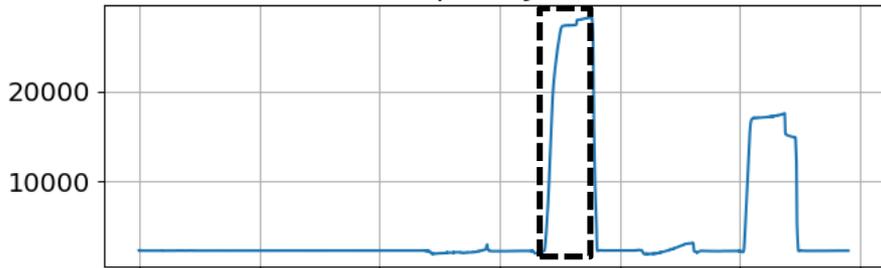
Temperature [°C] 20181109-RTV-S691.xlsx QCM 2



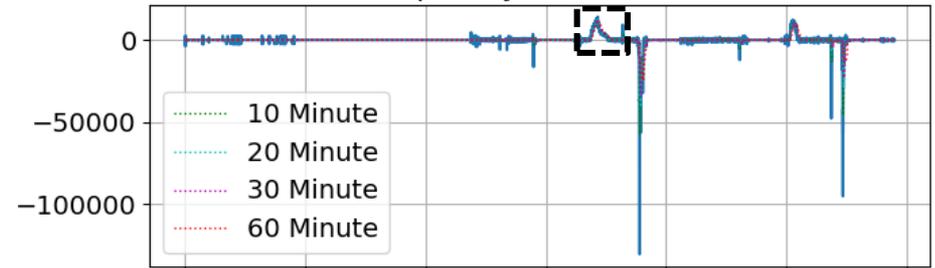
Test Time [Hours]



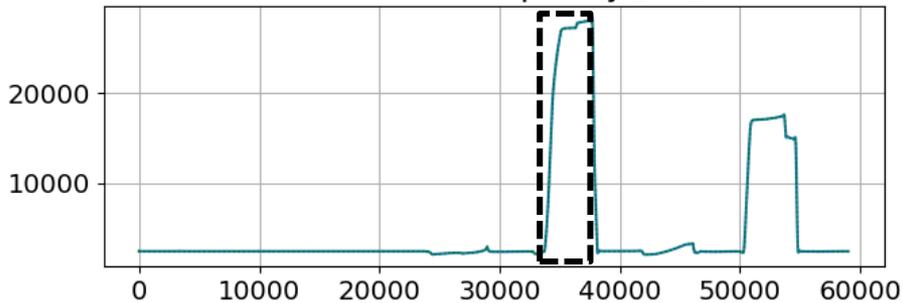
Frequency [Hz]



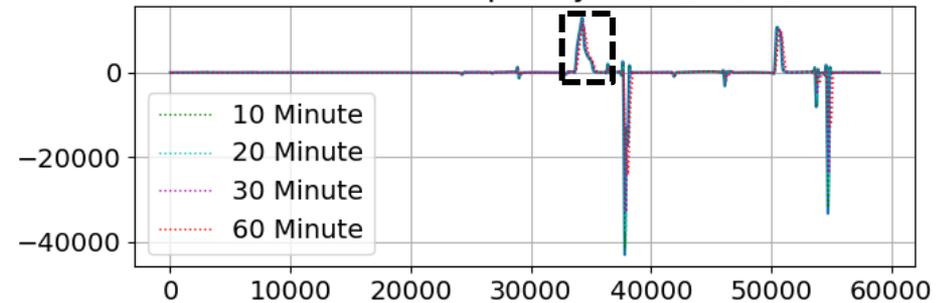
Frequency Rate [Hz/Hr]



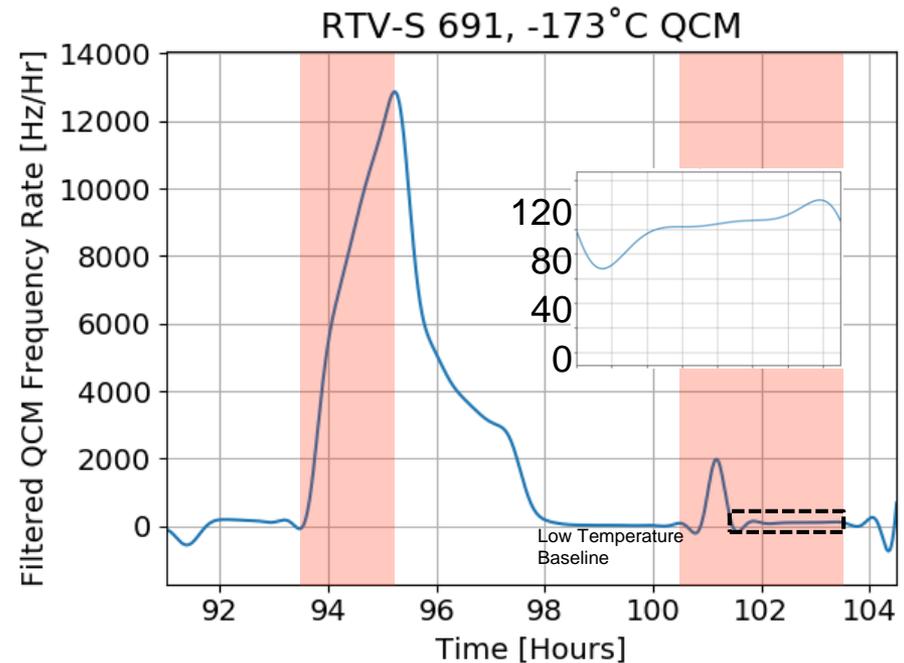
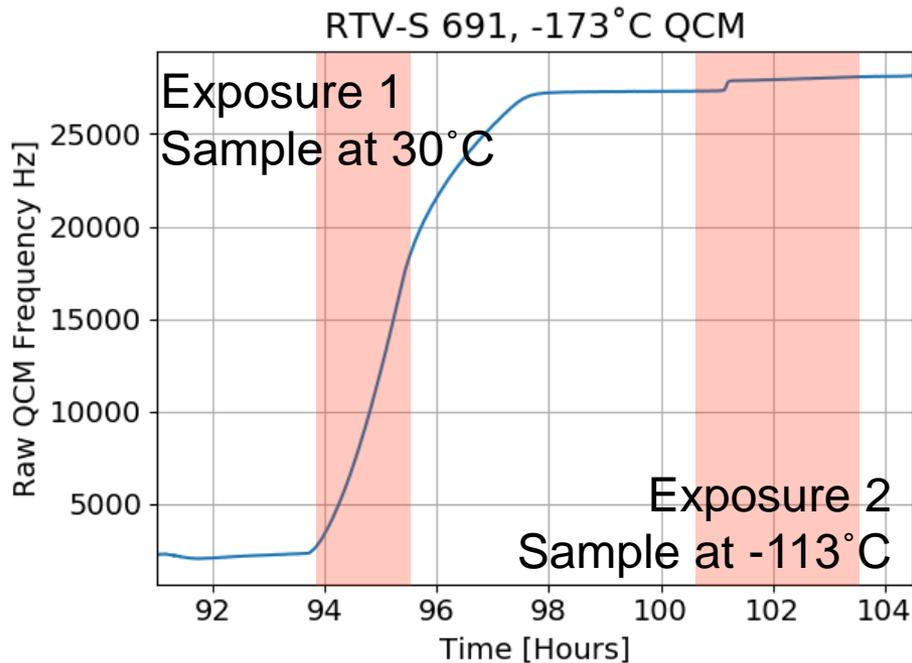
Smoothed Frequency [Hz]



Smoothed Frequency Rate [Hz/Hr]

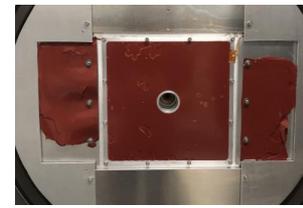


Expanded Test Section



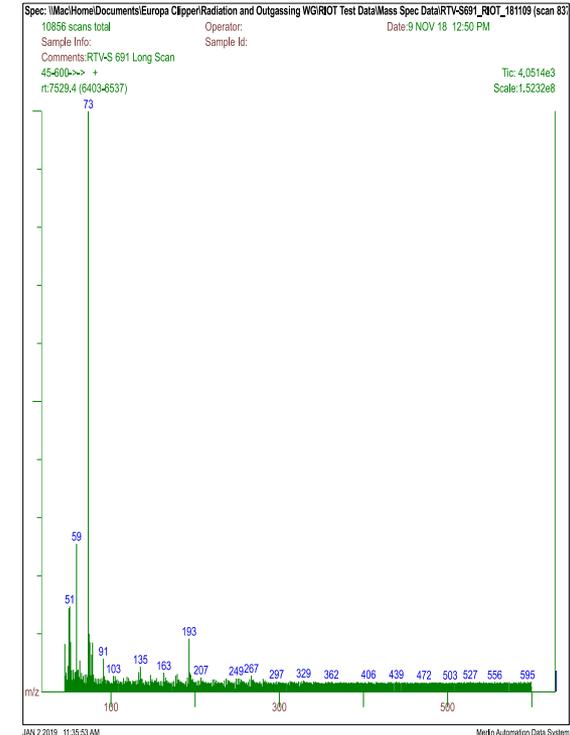
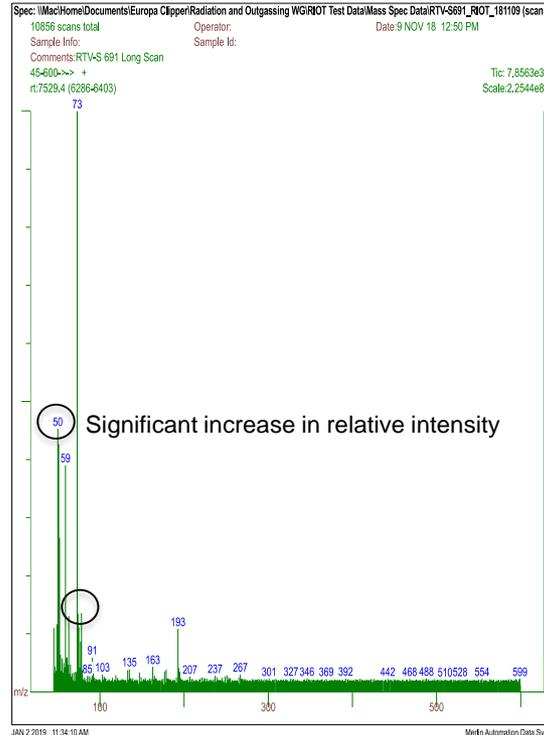
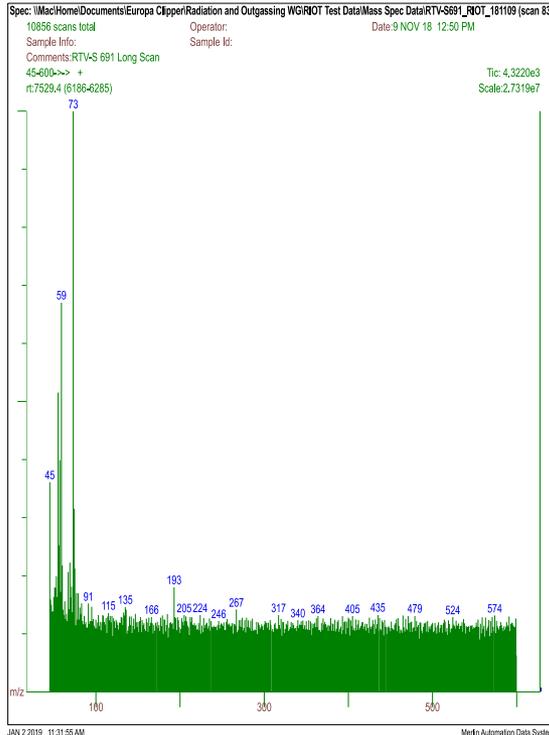
- Sample Temperature: +30°C
- Radiation exposure (1) at high temperature increases outgassing by orders of magnitude
- Termination of exposure 1 instantly begins decay of outgassing rate
- Low temperature radiation exposure (2) shows a more gradual but significant increase in outgassing rate above baseline levels

RTV-S 691 Mass Spectra Data Exposure 1

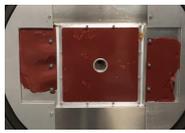


Wacker RTV-S 691

- Sample Temperature +30°C
- Relative intensities of species (50, 51, 52, 78 vs 73) change during irradiation
- Species during irradiation appear to be the same masses as without irradiation

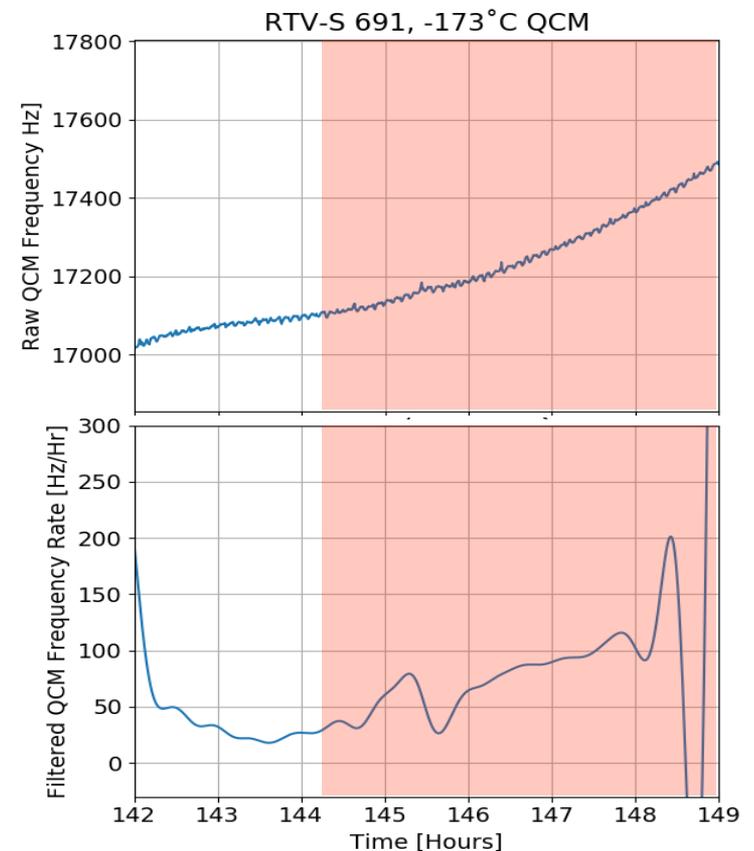
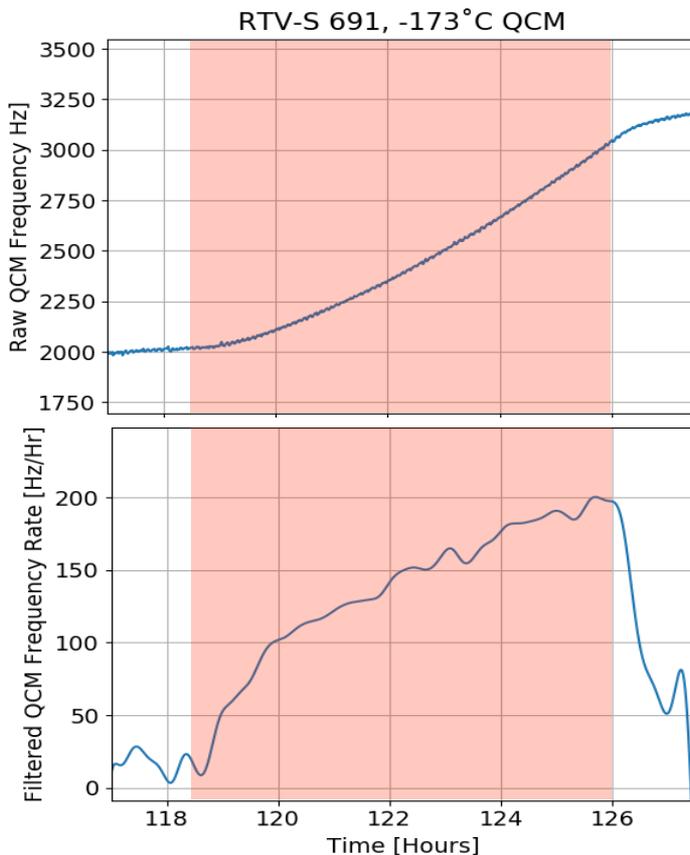


RTV-S691 Repeatability Checks at Low Temperature (Exposures 3&4)



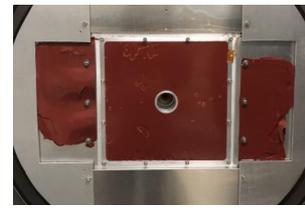
Wacker RTV-S 691

- Outgassing rates under irradiation approach approximately 200 Hz/Hr during both repeatability checks within an 8 hour exposure



Repeatability Chec

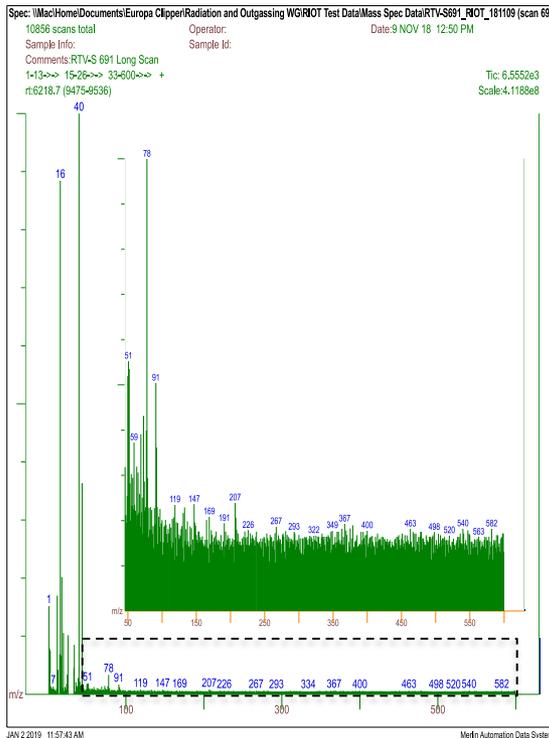
- Initial mass spectrum before irradiation has more pronounced silicone contaminant peaks
- Mass spectrum shows similar increases in contaminant peaks during and after irradiation
- Higher weight peaks appear after radiation than are seen before (281 specifically)



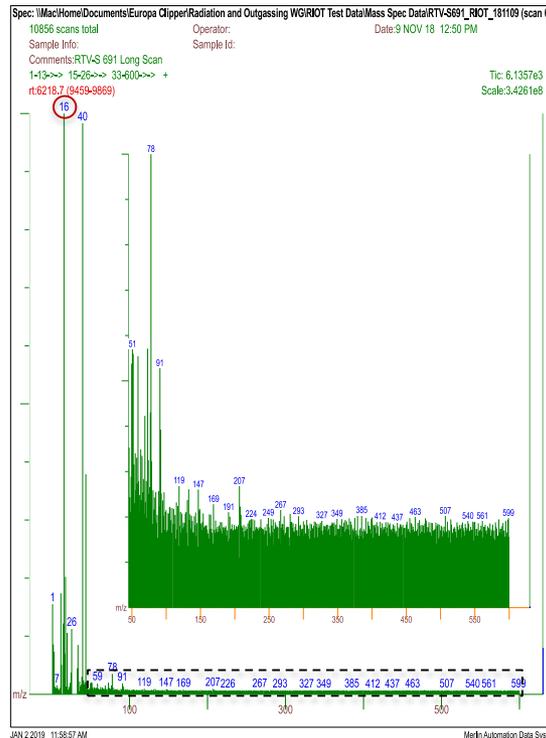
Wacker RTV-S 691

*scan range and MS tuning were change between these experiments

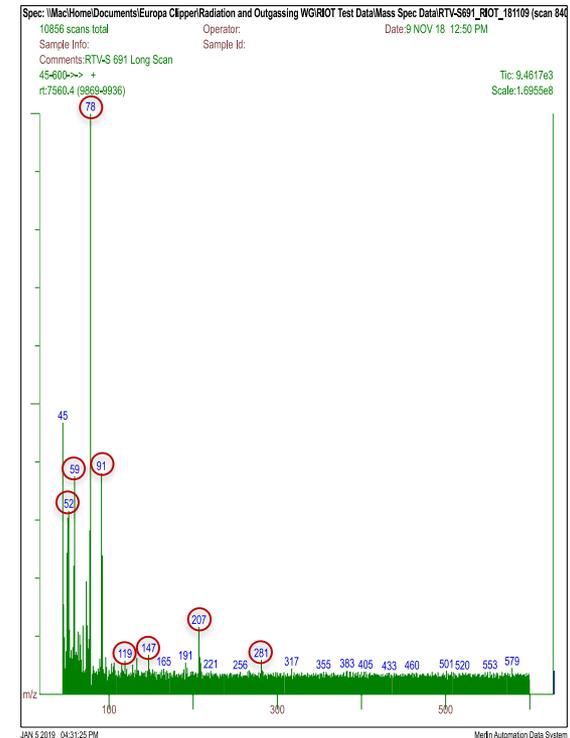
-113 °C Before Radiation



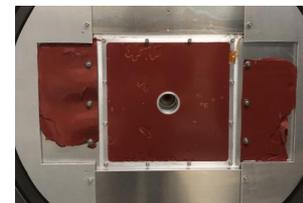
-113 °C During Radiation



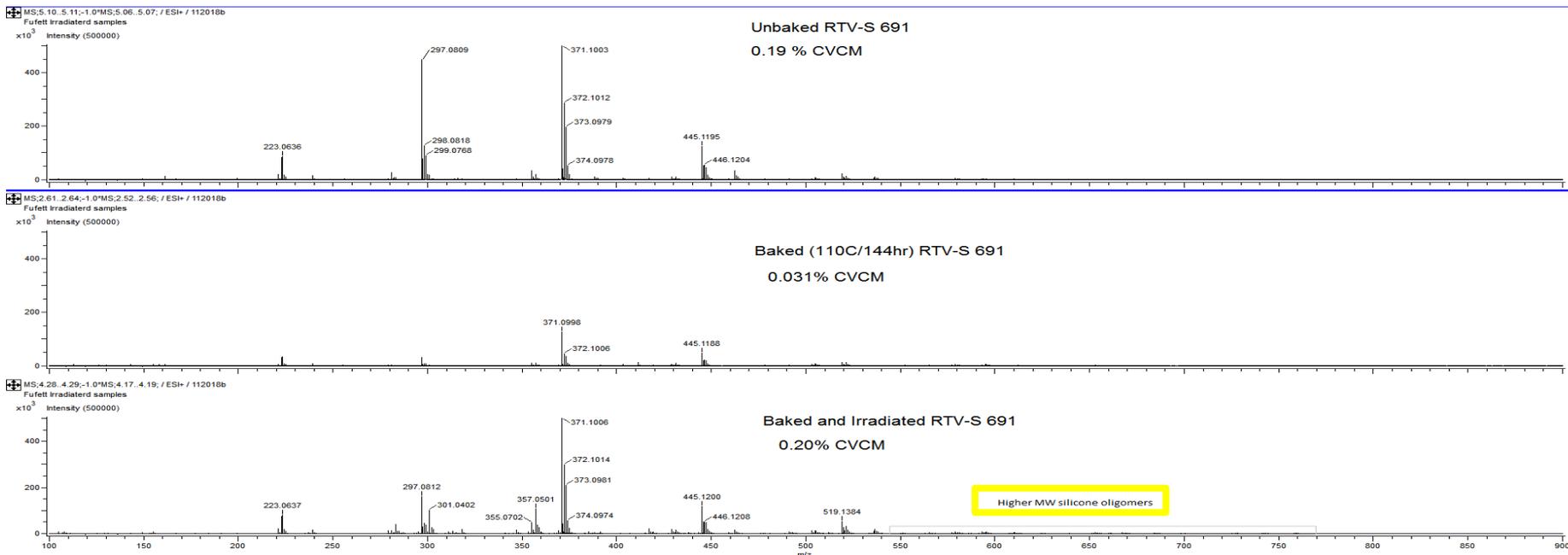
-113 °C After Radiation



Direct Analysis in Real Time (DART-MS) Results

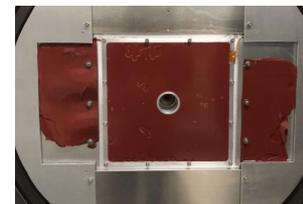


Wacker RTV-S 691

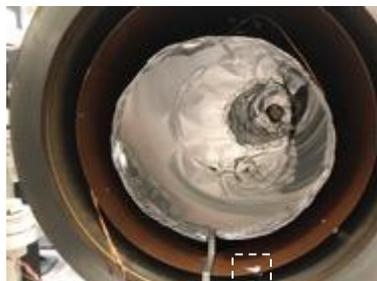


- DART-MS is a low energy mass spectrometry technique that yields primarily unfragmented parent species
- Analysis is of bulk material, may not be indicative of outgassed species
- Irradiated sample shows generation of high molecular weight (550 Da to 775 Da) silicone oligomers

DART-MS of Tenax Getter in Dynamitron Vacuum Chamber

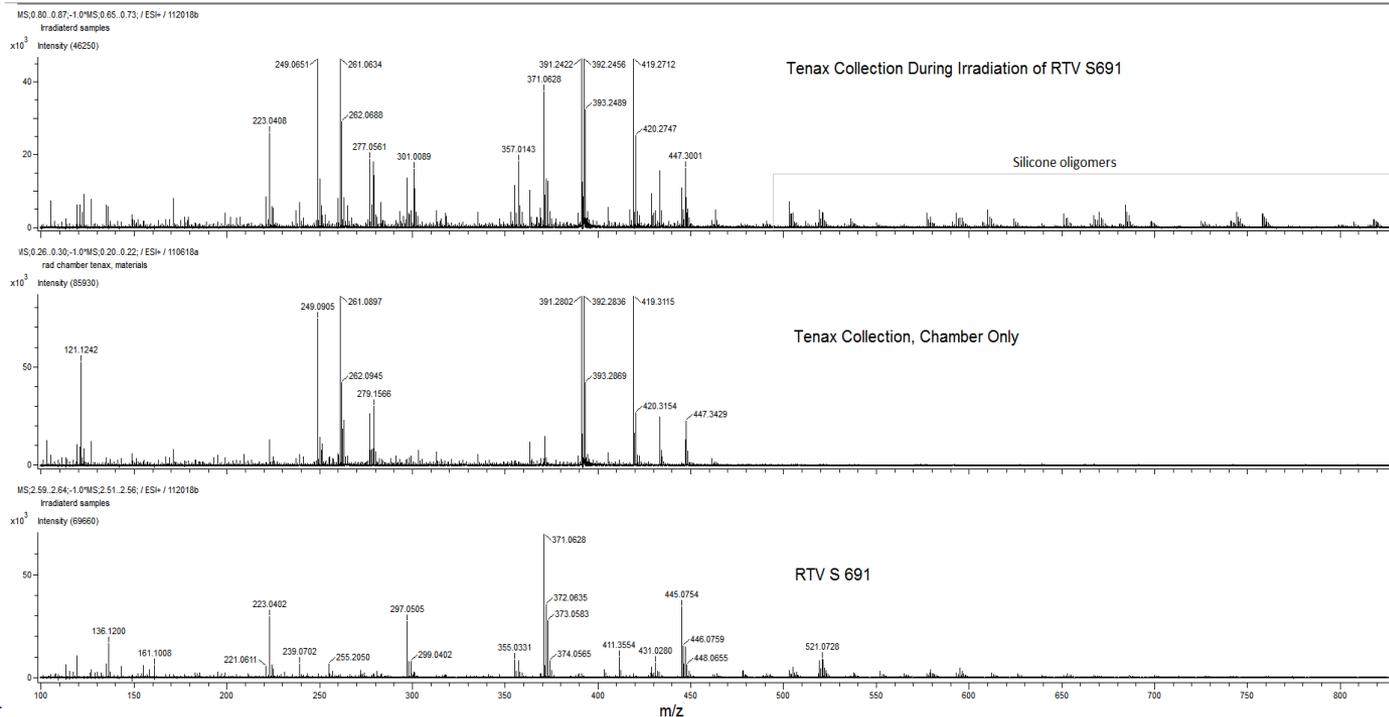


Wacker RTV-S 691

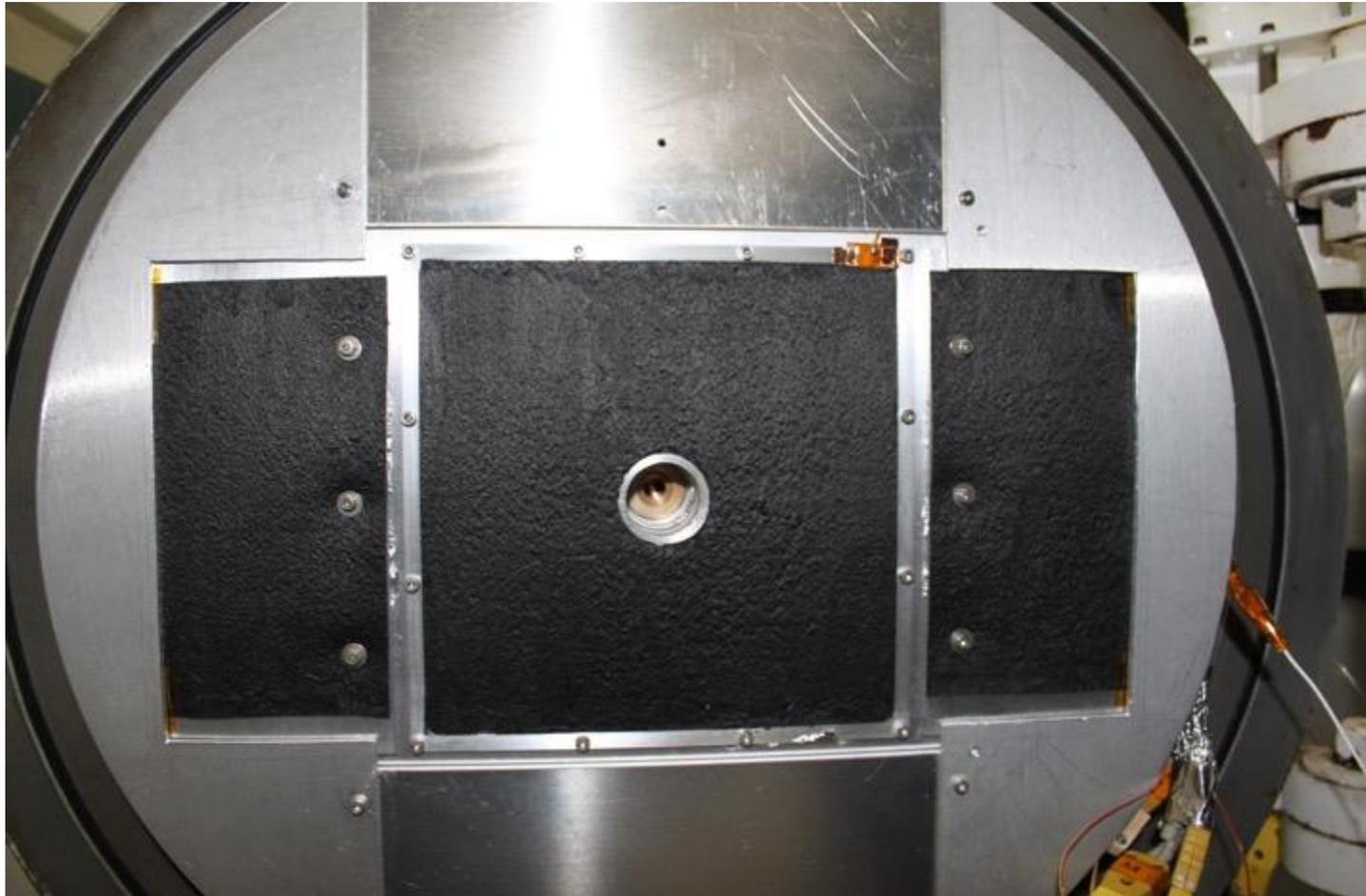


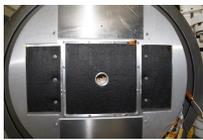
- Tenax molecular absorber was exposed in the Dynamitron vacuum chamber during RTV-S691 testing. A chamber run without RTV-S691 was previously run as a control.

- The Tenax collection during radiation (top) clearly shows the irradiated sample has a significant level of silicone oligomers being outgassed and collected in the Tenax. The chamber only run shows background volatiles (mid). For comparison, the RTV-S691 material analyzed directly by DART-MS



CV-1500 Conductive Silicone

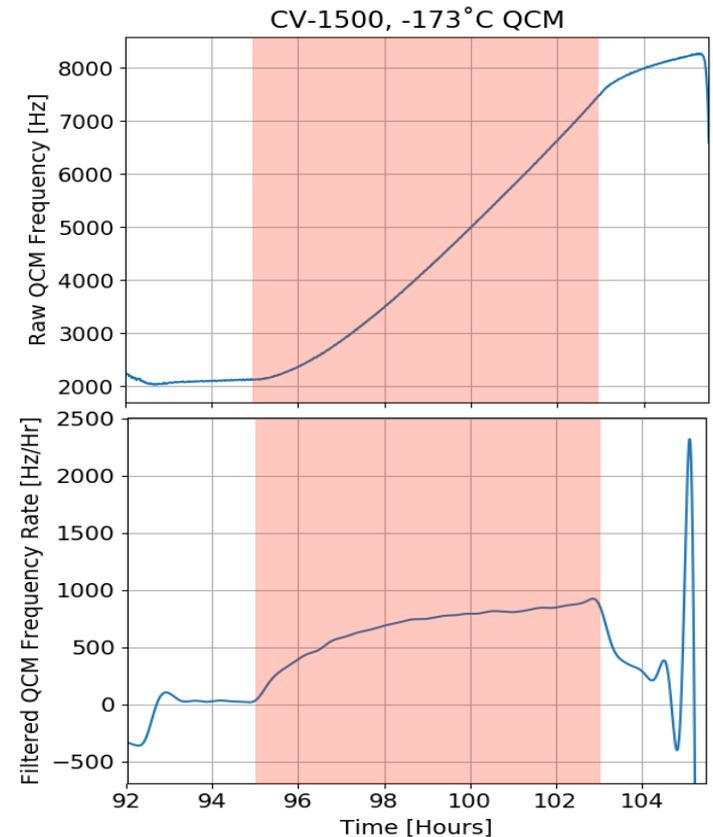
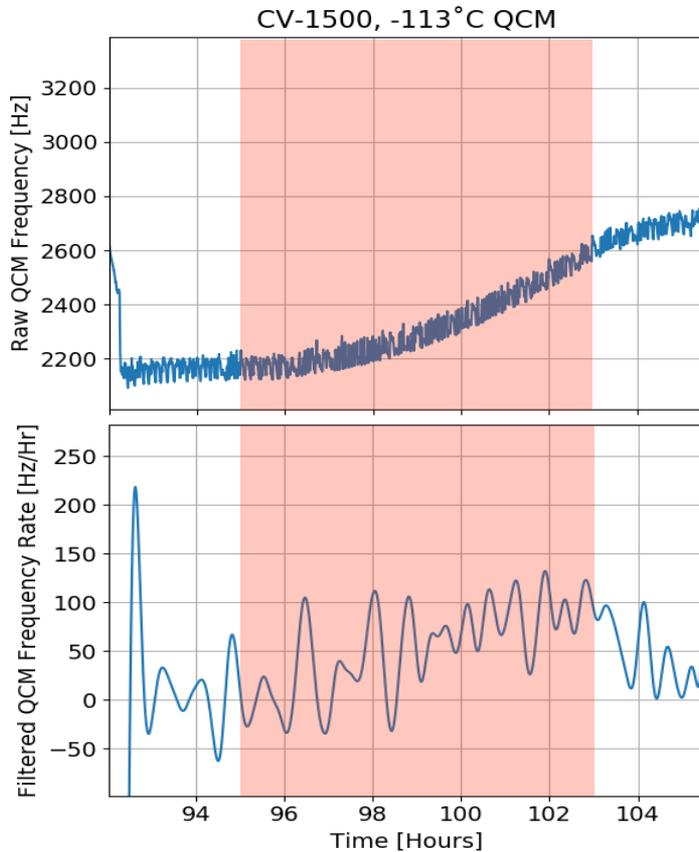




Nusil CV-1500

CV-1500

- Radiation exposure impacted Nusil CV-1500 stronger than any other material tested
- The -173°C QCM increased to 950 Hz/Hr
- The -113°C QCM increased to 100 Hz/Hr





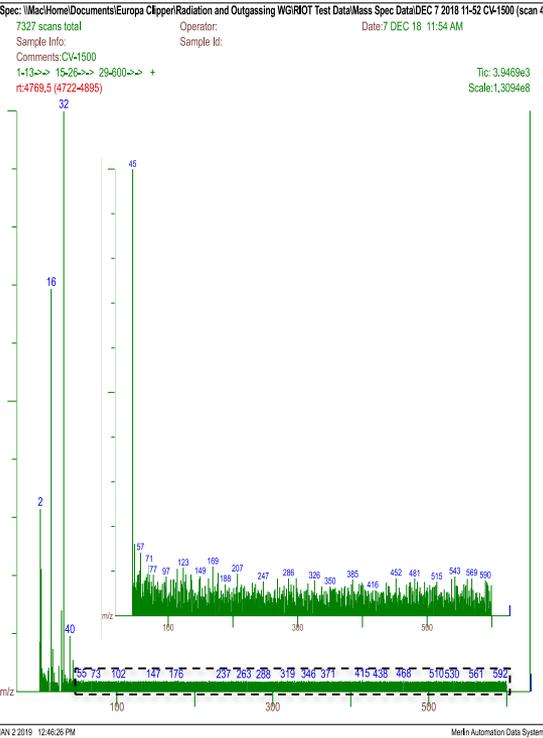
Nusil CV-1500

Mass Spectrometry for CV-1500

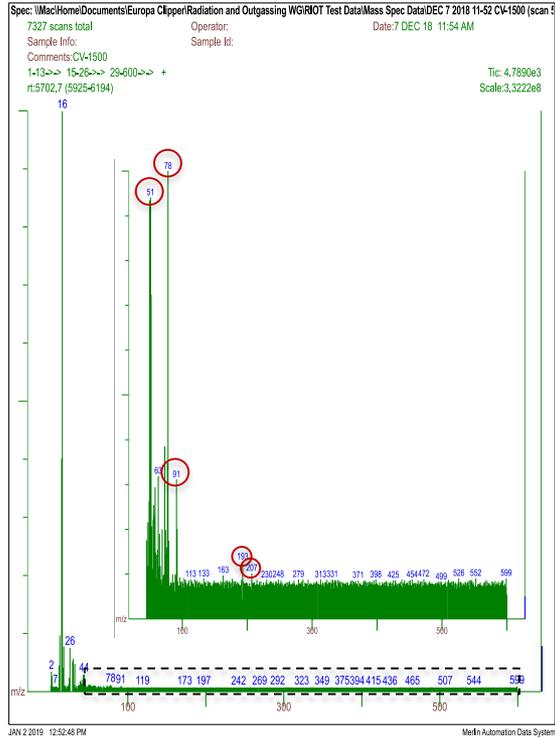
- CV-1500 shows evolution of MS peaks during and after radiation
 - silicones peaks ($m/z = 73, 91, 193, 207$)
 - Phenyl group peaks ($m/z = 50, 51, 52, 78$)

*scan range and MS tuning were change between these experiments

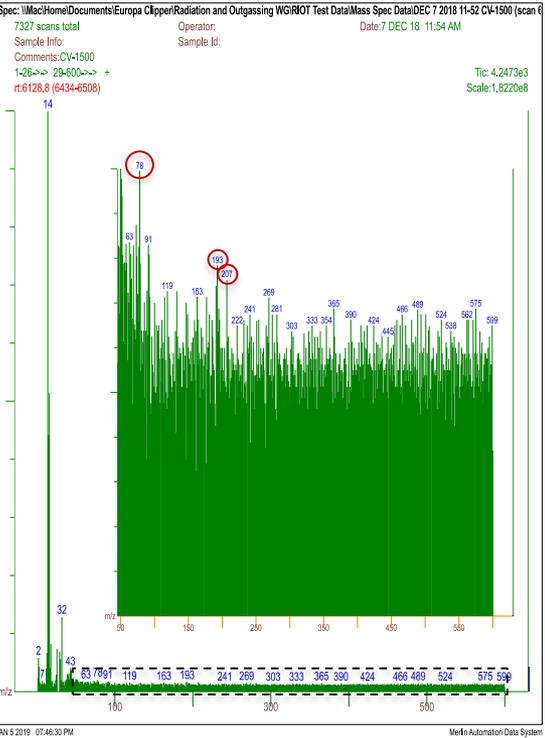
-113 °C Before Radiation



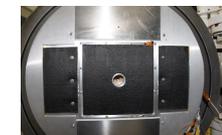
-113 °C During Radiation



-113 °C After Radiation



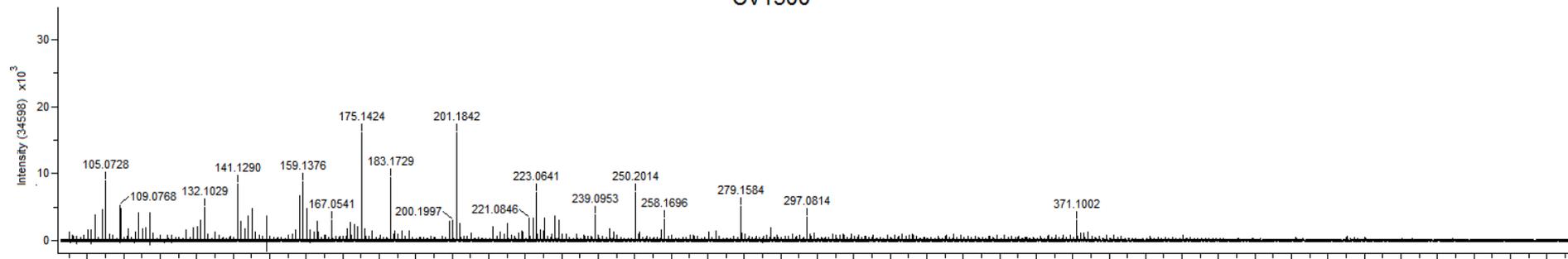
CV-1500 DART MS



Nusil CV-1500

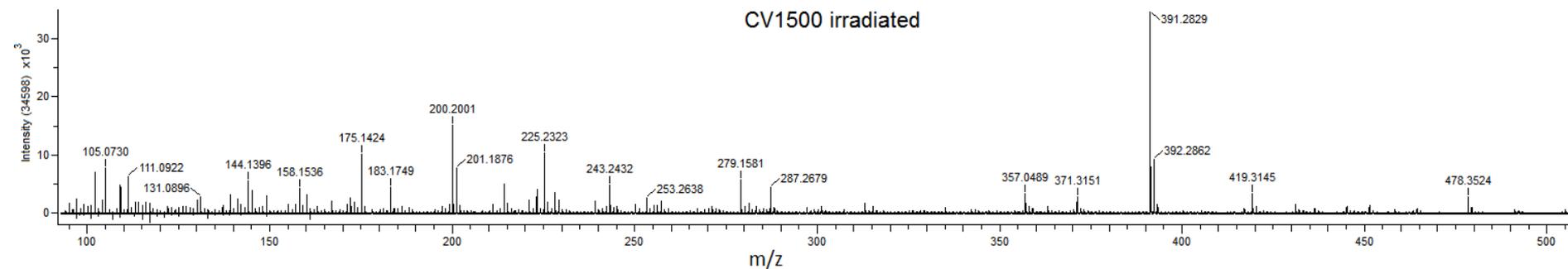
MS:5.00..5.05;-1.0*MS:4.62..4.72; / ESI+ / 121818b
A. Wong, RIOT

CV1500



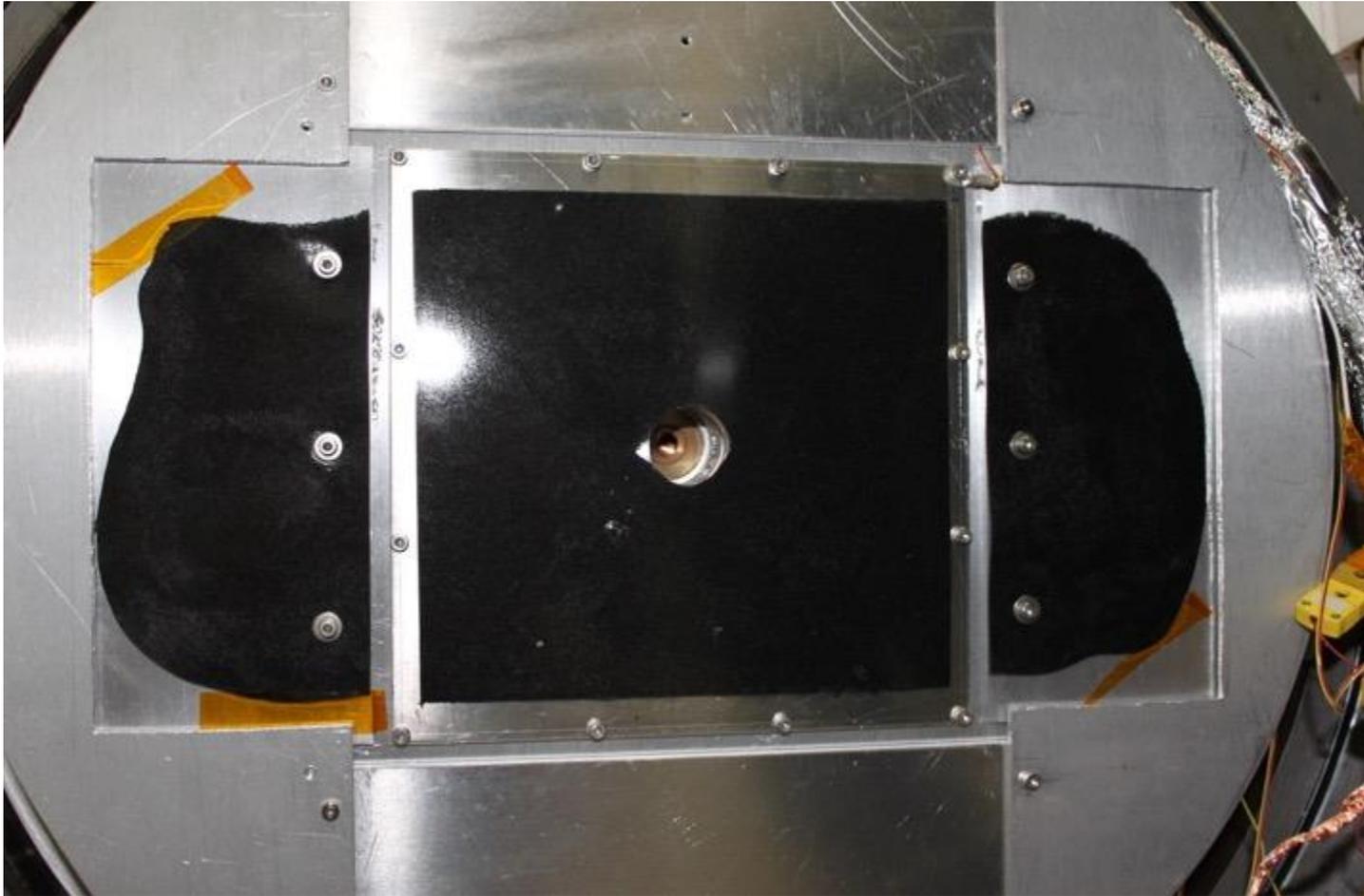
MS:5.73..5.84;-1.0*MS:5.35..5.49; / ESI+ / 121818b
A. Wong, RIOT

CV1500 irradiated

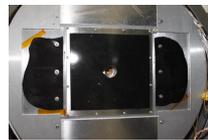


- Irradiated sample shows generation of high molecular weight (550 Da to 775 Da) silicone oligomers

SCV-2596

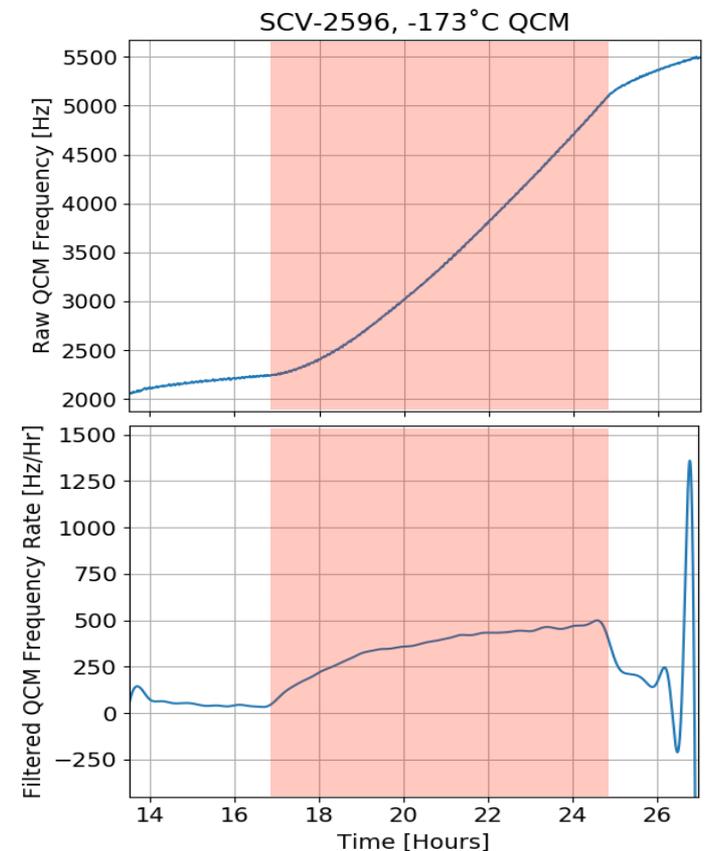
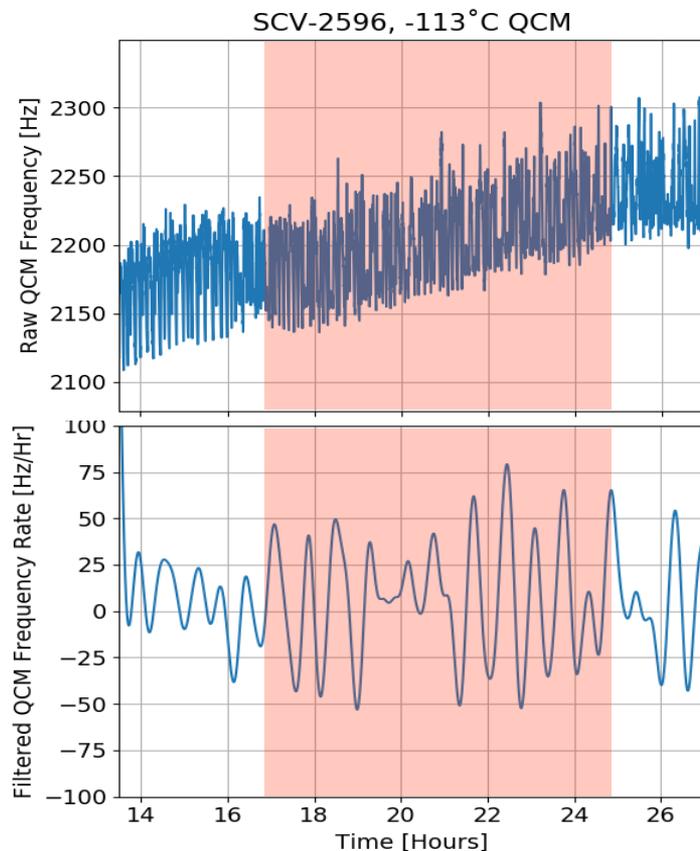


SCV-2596 Conductive Silicone

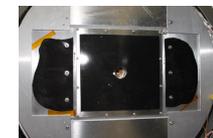


Nusil SCV-2596

- Super Controlled Volatility (SCV) is designed to be ultra low outgassing
- Radiation still increases outgassing rate by >10x
- The -173°C QCM increased to 500 Hz/Hr
- The -113°C QCM was not observed at any rate above background



Mass Spectrometry for SCV-2596

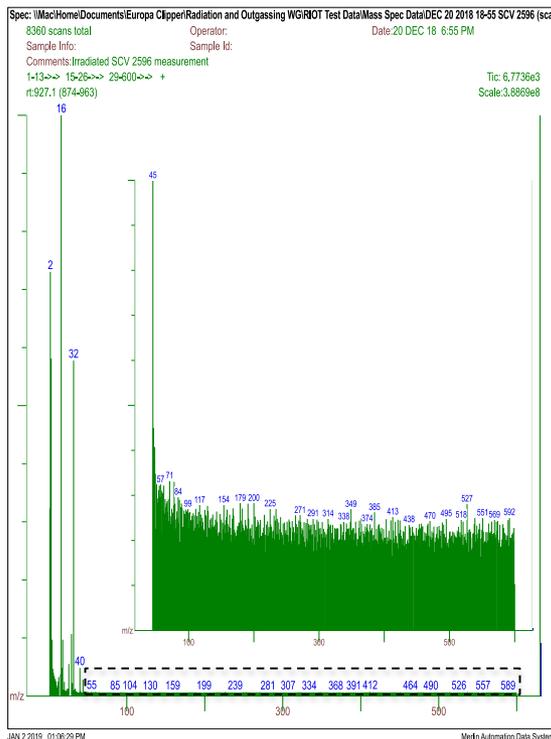


Nusil SCV-2596

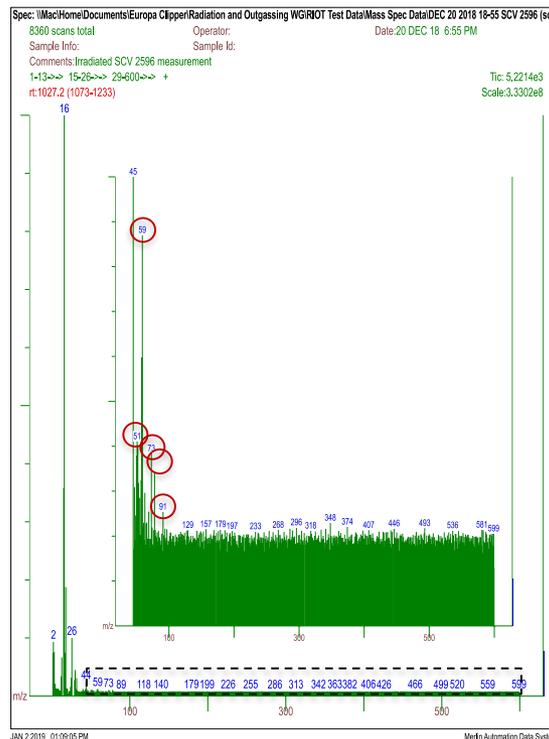
- SCV-2596 shows evolution of MS peaks
 - silicones peaks ($m/z = 73, 91$)
 - Phenyl group peaks ($m/z = 50, 51, 52, 78$)

*scan range and MS tuning were change between these experiments

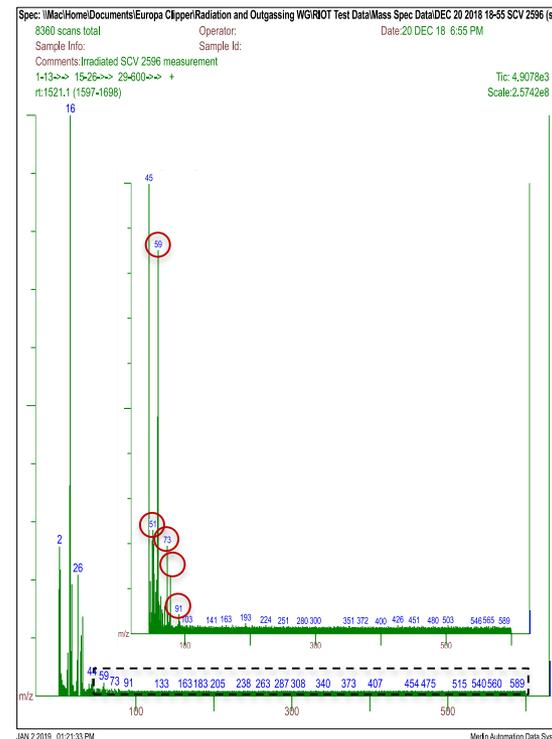
-113 °C Before Radiation



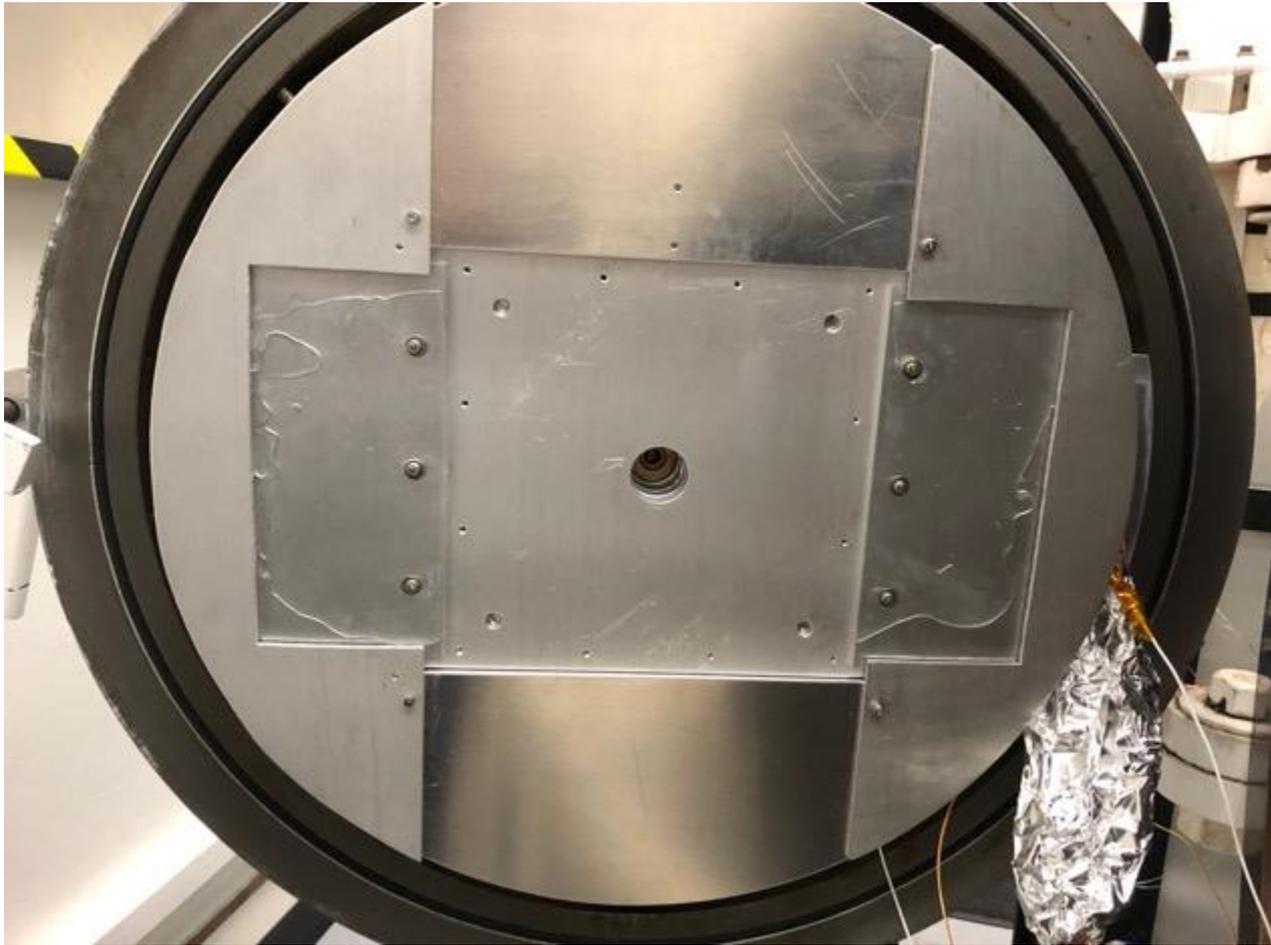
-113 °C During Radiation



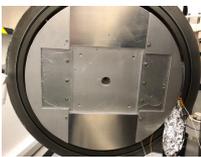
-113 °C After Radiation



SCV-2585

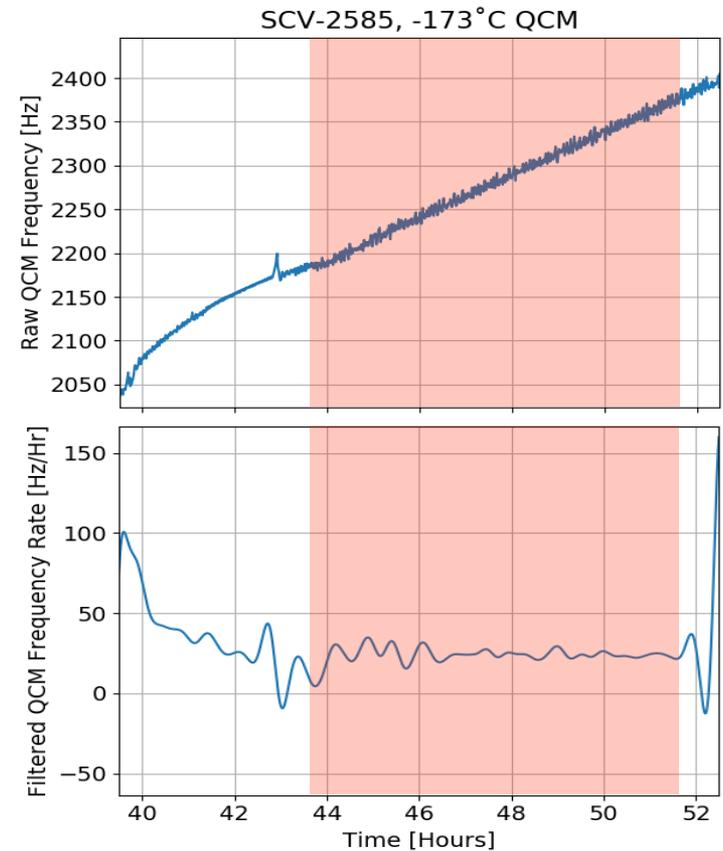
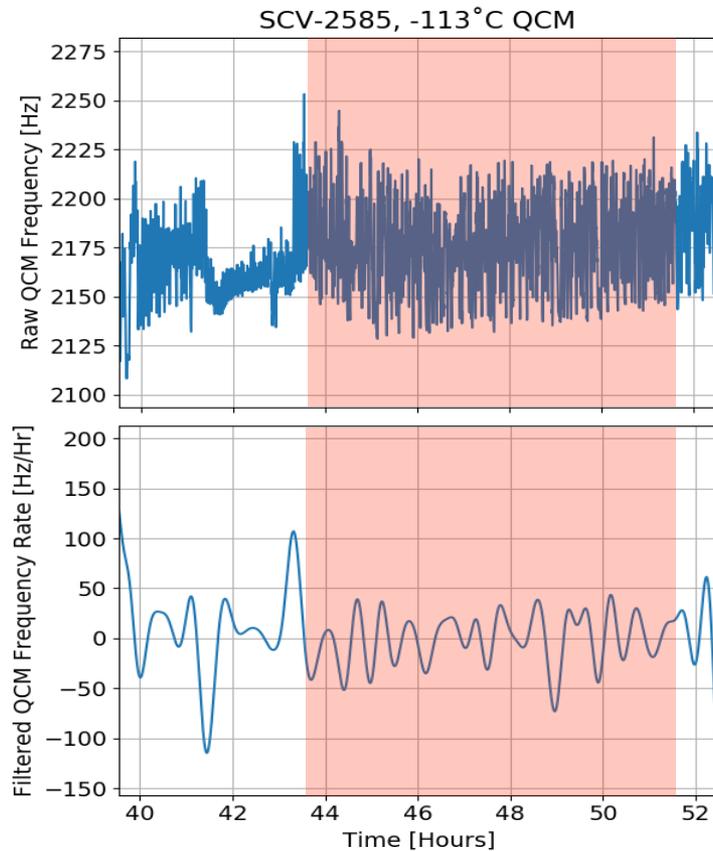


SCV-2585

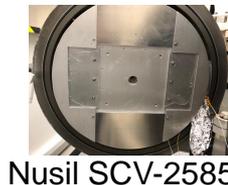


Nusil SCV-2585

- Radiation exposure impacted Nusil CV-1500 stronger than any other material tested
- Neither QCM signal changed above the background



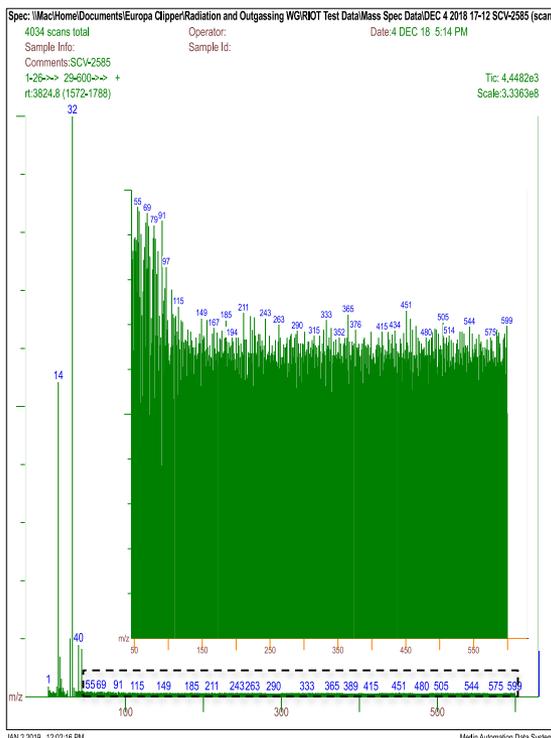
SCV-2585 Mass Spectrometry



- SCV-2585 shows no significant changes in MS peaks
 - Minor increase in Masses 46,69,78, and 119

*scan range and MS tuning
were change between these
experiments

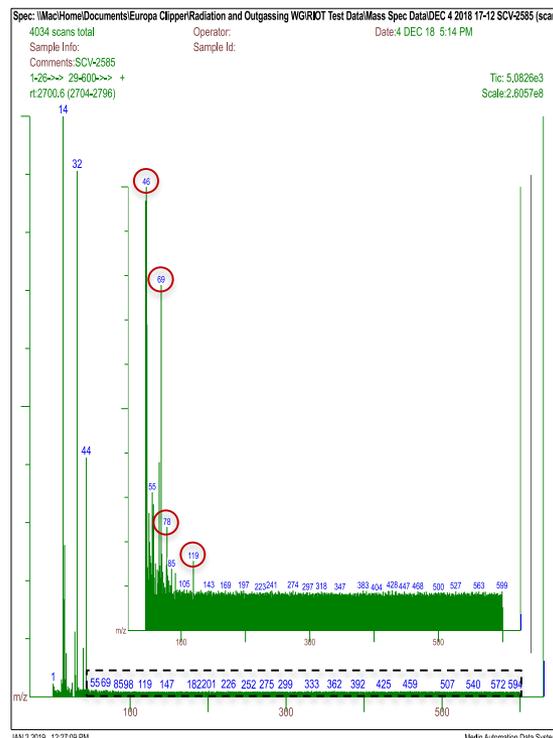
-113 °C Before Radiation



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MerIn Automation Data System

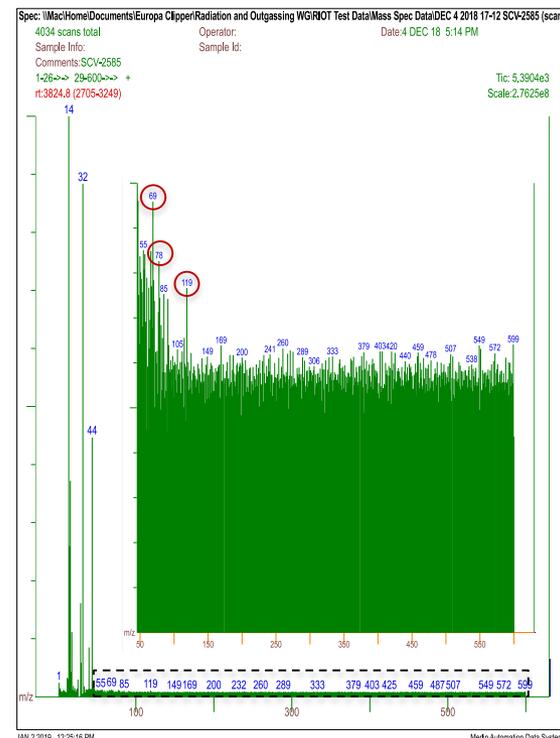
-113 °C During Radiation



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MerIn Automation Data System

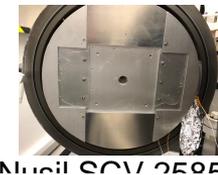
-113 °C After Radiation



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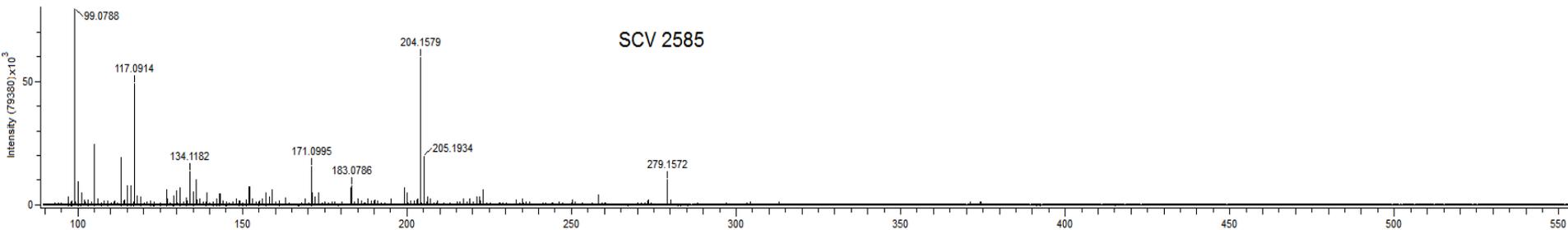
MerIn Automation Data System

SCV-2585 DART-MS

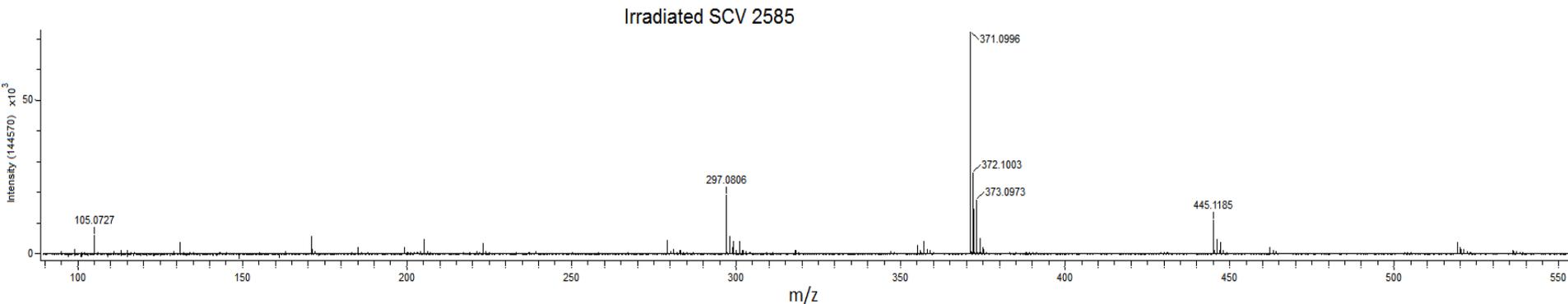


Model SCV 2585

MS; 2.86..2.90;-1.0*MS; 2.60..2.65; / ESI+ / 121818b
A. Wong, RIOT

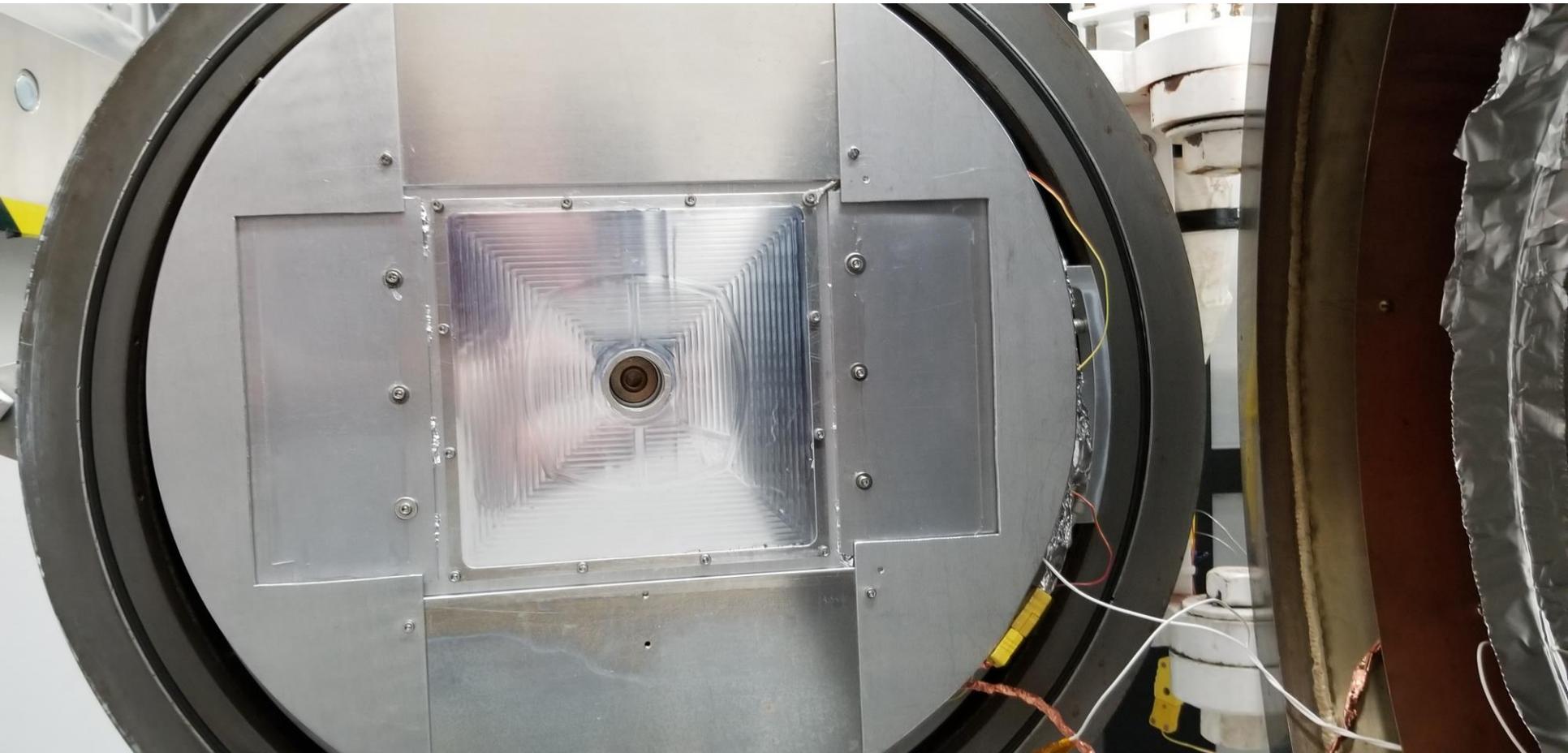


MS; 3.67..3.70;-1.0*MS; 3.54..3.62; / ESI+ / 121818b
A. Wong, RIOT

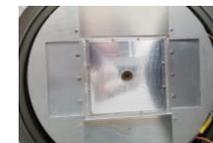


- Irradiated sample shows generation of high molecular weight (550 Da to 775 Da) silicone oligomers
- This increase is not reflected in the outgassing measurements

DC 93-500

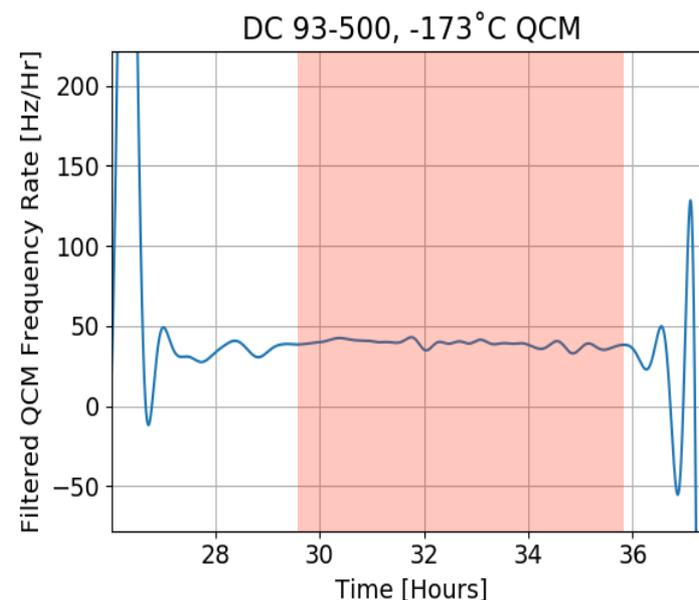
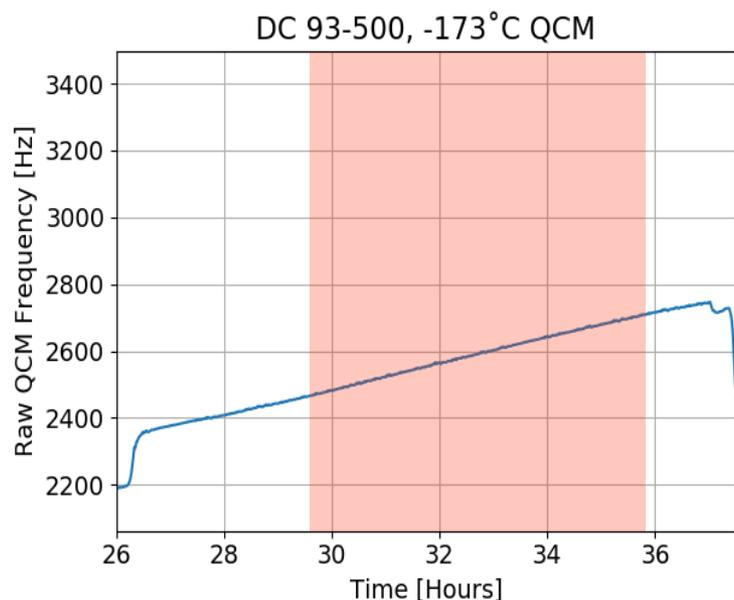


DC 93-500

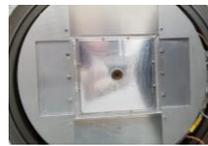


DC 93-500

- 8 Hour Exposure demonstrates no change in outgassing rate
- Outgassing rate remains at background level for both QCMs



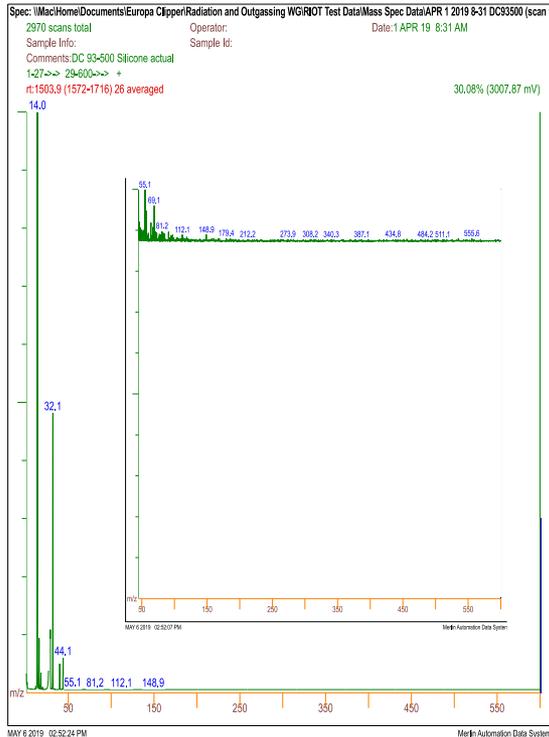
Mass Spectrometry for DC 93-500



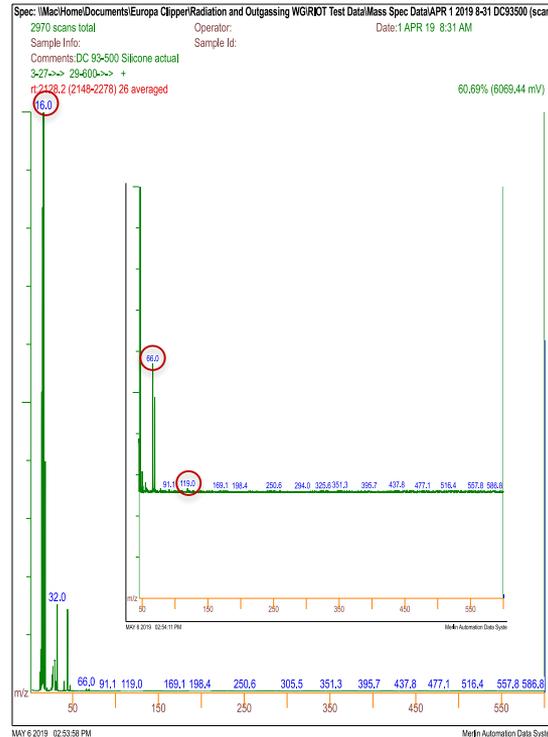
DC 93-500

- DC 93-500 shows no significant changes in MS peaks
 - Minor increase in Masses 66 and 119

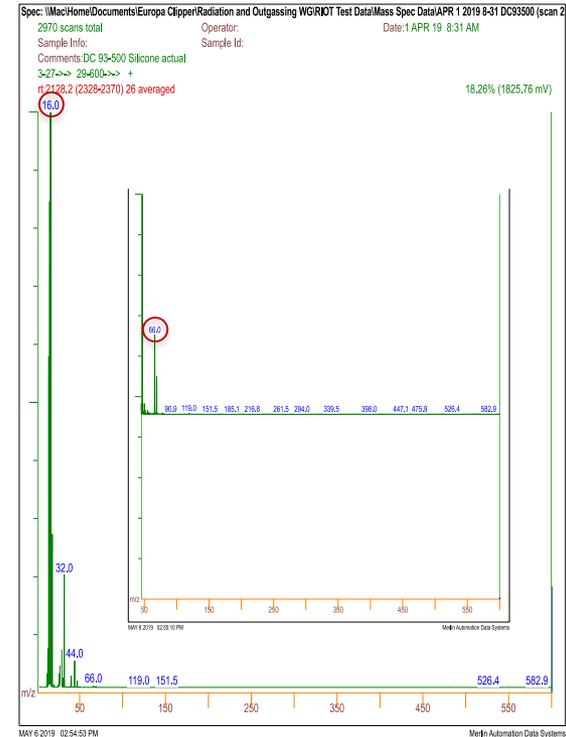
-113 °C Before Radiation



-113 °C During Radiation



-113 °C After Radiation

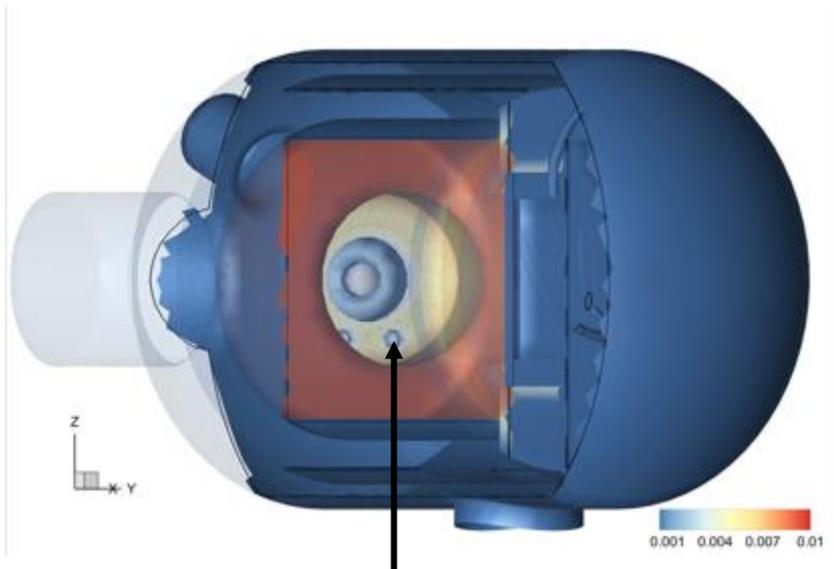


Transport Factor Bounding Cases

Analytic: 0.045%

Calculated by creating geometric model of chamber and modeling molecular flow from sample

ASEC Presentation on Friday at 8:50 am by Dr. William Hoey



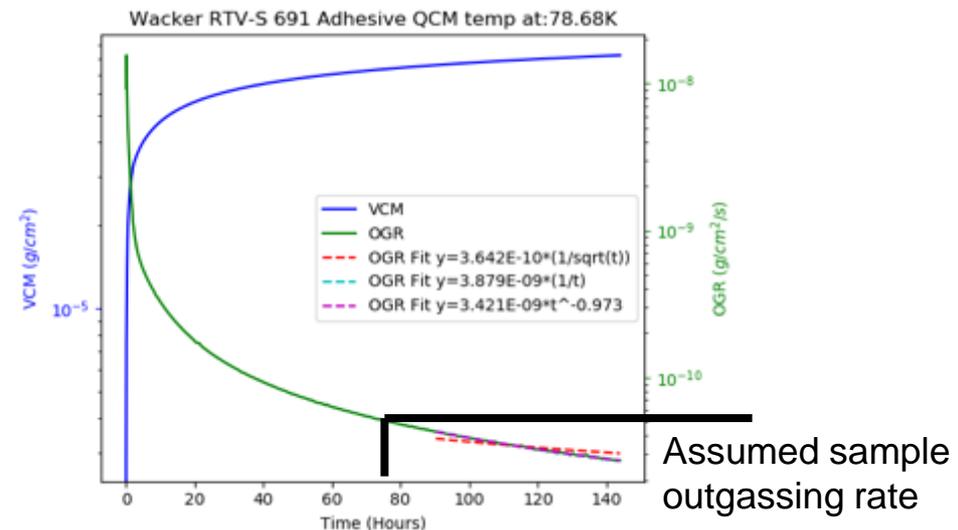
Transport factor calculated to QCM surfaces

Experimental: 0.28%

Calculated by comparing ASTM-E1559 data to chamber measurements

Assumptions:

- Sample has outgassing rate as measured by ASTM-E1559
- Chamber 100K QCM collects the same material as ASTM-E1559's 80K QCM



Combined Results of RIOT Testing

-173°C QCM Results

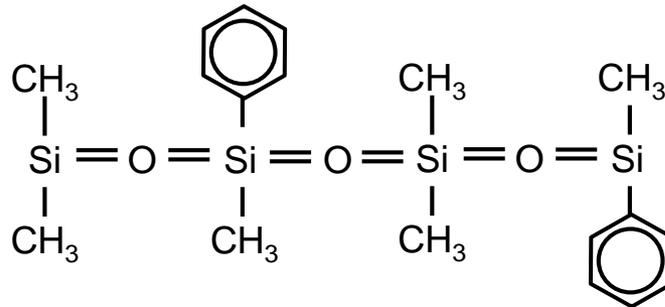
| Silicone Sample | Sample Color | Primary Property | Final Irradiated Outgassing Rate [Hz/Hr] |
|------------------|--------------|----------------------|--|
| Wacker RTV-S 691 | Red | Yield Strength | ~200 |
| Nusil CV-1500 | Black | Conductive | ~950 |
| Nusil SCV-2596 | Black | Conductive | ~500 |
| Nusil SCV-2585 | Clear | Yield Strength | ~25 (Background) |
| DC 93-500 | Clear | Optical Transparency | ~40 (Background) |

Mass Spectra Results

| Silicone Sample | Mass Signal Increases Due to Irraditaion | Identified Species |
|------------------|---|---------------------------------|
| Wacker RTV-S 691 | 16, 50, 51, 52, 78, 59, 91, 147, 207, 281 | Oxygen, Silicones, Phenyl Group |
| Nusil CV-1500 | 16, 50, 51, 52, 78, 92, 193, 207 | Oxygen, Silicones, Phenyl Group |
| Nusil SCV-2596 | 16, 51, 59, 73, 78, 91 | Oxygen, Silicones, Phenyl Group |
| Nusil SCV-2585 | 16, 46, 69, 78, 119 | Oxygen, |
| DC 93-500 | 16, 66, 119 | Oxygen, Silicones |

Conclusions

- Pure Silicone materials (SCV-2585 and DC 93-500) demonstrated no increase in outgassing from radiation exposure
- Materials with filler (RTV-S691, CV-1500, SCV-2596) all showed continuous increases with respect to time during radiation exposure
- Outgassing rates fall off when radiation exposure is terminated
- Mass Spectra of irradiated samples yield the same mass constituents (no new species) but at different relative intensities





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Backup: Proposed Mechanism

- Bond scission can occur at any bond in the silicone structure
- Functional groups break off and diffuse quickly out of the bulk
- Silicone backbone breaks but diffuses more slowly
- Breaks in the silicone backbone create radical sites that can recombine

