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# **Aluminum and Other Coatings for the Passivation of Tritium Storage Vessels**

**William A. Spencer**

**Paul S. Korinko**

**September 2016**

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Dien Li who led the nano diamond research effort,

Edward Stein and Brent Peters, for vacuum bake-out and vessel assembly

Dale Hitchcock for aluminum vessels

## EXECUTIVE SUMMARY

Using a highly sensitive residual gas analyzer, the off gassing of hydrogen, water, and hydrocarbons from surface treated storage vessels containing deuterium was measured. The experimental storage vessels were compared to a low off-gassing, electro-polished 304L canister. Alternative vessels were made out of aluminum, or were coatings on 304L steel. Coatings included powder pack aluminide, electro-plated aluminum, powder pack chromide, dense electro-plated chromium, copper plated, and copper plated with 25 and 50 percent nano-diamond. Vessels were loaded with low pressure deuterium to observe exchange with protium or hydrogen as observed with formation of HD and HDO. Off gas of D<sub>2</sub>O or possible CD<sub>4</sub> was observed at mass 20. The main off gas in all of the studies was H<sub>2</sub>.

The studies indicated that coatings required significant post coating treatment to reduce off gas and enhance the permeation barrier from gases likely added during the coating process. Dense packed aluminum coatings needed heating to drive off water. Electro-plated aluminum, chromium and copper coatings appeared to trap hydrogen from the plating process. Nano-diamond appeared to enhance the exchange rate with hydrogen off gas and its coating process trapped significant amounts of hydrogen. Aluminum caused more protium exchange than chromium treated surfaces. Aluminum coatings released more water but pure aluminum vessels released small amounts of hydrogen, little water, and generally performed well. Chromium coating had residual hydrogen that was difficult to totally outgas but otherwise gave low residuals for water and hydrocarbons.

Our studies indicated that simple coating of as received 304L metal will not adequately block hydrogen. The base vessel needs to be carefully out gassed before applying a coating and the coating process will likely add additional hydrogen that must be removed. Initial simple bake out and leak checks up to 350° C for a few hours was found to be inadequate. All of the studies indicated that vessels needed several days of vacuum baking at 350-450° C to fully outgas the residual gases, which were mostly hydrogen.

The current standard practice of out gassing from ultra-clean, electro-polished 304L vessels with both vacuum bake out and followed by an oxidative bake out to enhance the chromium surface performed the best in these studies.



## TABLE OF CONTENTS

LIST OF TABLES.....	x
LIST OF FIGURES .....	xi
LIST OF ABBREVIATIONS.....	xiii
1.0 Introduction.....	1
2.0 Experimental Procedure.....	5
2.1 Aluminizing and Chromizing.....	5
2.2 Chrome Plating.....	6
2.3 Plating processes for ND coatings.....	6
2.4 SEM and EDX Characterization .....	6
2.5 Test Vessels:.....	7
2.6 Mass Spectrometry Experimental Test Procedure: .....	10
2.7 Tube Furnace for Vacuum Baking .....	12
2.8 LIBS Measurements .....	12
3.0 Results and Discussion .....	12
3.1 Coating Characterization.....	12
3.2 Thermal Evolution of Outgas from 304L Steel.....	16
3.3 Individual tests with deuterium .....	18
3.4 Vacuum Bake-out.....	25
3.5 Data Summaries .....	28
3.6 Aluminum Housings and Vessels.....	37
4.0 Conclusions.....	39

5.0 Recommendations, Path Forward or Future Work ..... 40

6.0 References..... 41

7.0 Appendix..... 44

8.0 Distribution: ..... 1

## LIST OF TABLES

Table 1 Milestones for PDRD 2015-2016 .....	2
Table 2 Coating composition in percent for alumide and chromide coatings.....	13
Table 3 Tube Furnace Bake out Summary.....	28
Table 4 Off gas Rates for Selected Ion Mass (m) – Units of mbar <sub>l</sub> /s <sub>cm</sub> <sup>2</sup> .....	44

## LIST OF FIGURES

Figure 1 Typical appearance of an as-received (left) and commercially electropolished (right) pipe.....	1
Figure 2 Photograph of Gas Bottle Assembles (a) Type 304L SS (b) Type 304L SS Commercially EP (c) Cr plated Type 304L SS (d) Cr plated Type 304L SS Commercially EP (e) Swagelok 500 ml Type 304L bottle, (f) Chromized Swagelok 500 ml Type 304L bottle, (g) aluminized Swagelok 500 ml Type 304L bottle, (h) electroless plated Cu or Cu-ND on Type 304L SS.....	8
Figure 3 100 mL vessels with copper, nano-diamond, chrome, and steel treatments.....	9
Figure 4 External surface appearance of Praxair aluminized and chromized coatings compared to standard Type 304L SS gas sample bottles. ....	10
Figure 5 Aluminide layer .....	13
Figure 6 Chromide layer .....	13
Figure 7 Surface appearance of the Cr plated CF blank flange at low and high magnification. The coating holiday does not appear to extend through the thickness based on the lack of Fe signal in the EDS X-ray map. ....	14
Figure 8 EDS of aluminide coating.....	15
Figure 9 EDS of chromide coating. ....	15
Figure 10 Evolved off gas from stainless steel shim stock that was saturated in 2.5 atm hydrogen at 500°C per selected mass ion. ....	17
Figure 11 Deuterium Standard the small signal at mass 2 is D instead of H <sub>2</sub> . A trace HD was observed at mass 3 and residual water and air varied depending on loading day.....	20
Figure 12 Spectra of untreated Type 304L stainless steel CFVA had noticeable HD formation and some CO.....	21
Figure 13 Electro-polished Type 304L SS CFVA was similar to Type 304L SS but less CO and residuals. HD formation was observed in most of the stainless steel CFVA indicating presence of exchange sites. ....	22
Figure 14 The Cu-25% ND coated CFVA had so much hydrogen off-gas that the initial deuterium load was minor. HD appeared to be near at equilibrium with the H and D mix. The hydrogen ingrowth was due to the electroless copper ND coating process. ....	23

Figure 15 Electro-plated chrome coated CFVA showed significant hydrogen off gas in the as received condition but exhibited little HD formation. Hydrogen was generated and diffused during coating process. .... 24

Figure 16 The Restek Electro-polished gas sample bottle contained the deuterium at nearly the same composition as the initial standard. The Siltek gas sample bottle exhibited similar behavior. .... 25

Figure 17 ..... 27

Figure 18 ..... 27

Figure 19 ..... 27

Figure 20 Hydrogen Off gas Rate ..... 30

Figure 21 HD Off gas Rate ..... 32

Figure 22 Some of the test containers had air leakage. To see the effect the larger H2 and HD data is not shown in this data set. .... 34

Figure 23 Baking out clearly reduced residual water in the samples and some coatings held water..... 36

Figure 24 Aluminum housing was used for the mass spectrometer..... 37

Figure 25 Cross Sectional view for a potential all aluminum 3 liter expansion volume. .... 39

## LIST OF ABBREVIATIONS

CF	ConFlat(TM) Flange
CVD	Chemical Vapor Deposition
DI	Deionized
EDX	Energy Dispersive X-ray Spectroscopy
ICP-OES	Inductively Coupled Plasma–Optical Emission Spectroscopy
ND	Nano-diamond
PDRD	Plant-Directed Research and Development
PSD	Particle Size Distribution
SEM	Scanning Electron Microscope
SRNL	Savannah River National Laboratory
SRTE	Savannah River Tritium Enterprise
CFVA	ConFlat Flanged Vessel Assembly
CTCV	Commercial Tritium Containment Vessel
SecEM	Secondary Electron Multiplier (as used on the MS)
MS	Mass Spectrometry
STP	Standard Temperature and Pressure (25°C, 1 atm)

## 1.0 Introduction

Savannah River Tritium Enterprise (SRTE) has several applications that require passivated surfaces for hydrogen isotope storage or for analytical systems. These applications generally utilize surfaces that are passivated by proprietary processes and include mass spectrometer housings, inlet manifolds, expansion volumes, gas standards bottles, piping, and valves. Recently the proprietary process has proven unreliable, likely, due to generational changes at the vendor as well as new sources for stainless steel. In addition, the preferred vendor has recently ceased operations.

This Plant Directed Research and Development project sought to develop alternative materials and methods for tritium storage compared to the currently accepted electro-polish and heat treatments being used. The benefits and progress to date are an aluminum vacuum manifold component that reduced the residual (background) pressure by a factor of 20 and new test bottles with aluminized, chromized, and nano-diamond surfaces.

Based on the successful reduction in off gassing from an evacuated bottle, the test vessels will be transferred to tritium laboratories for testing with hydrogen and tritium. In addition, an aluminum expansion volume has been designed for evaluation on an SRTE process mass spectrometer. New vessels meeting appropriate SRTE specifications are expected from these studies. Additional tests with variations of electro-polishing, heat treatments, and plating options are being pursued under a separate project to further explore options for limiting hydrogen exchange in storage vessels. This report describes tests results and new test and evaluation procedures that were developed during the project.

*Due to challenges in obtaining properly “passivated” stainless steel commercial tritium containment vessels (CTCV) as well obtaining high quality passivated inlet system components, a number of projects to better understand and develop new methods were proposed and funded. This project, in particular, will test and deploy alternative materials and coatings for tritium gas standards and for mass spectrometer inlet manifolds. This research and development is needed to understand the limits of the new technologies and techniques as well as to determine their suitability for future applications.*



Figure 1 Typical appearance of an as-received (left) and commercially electropolished (right) pipe.

Tritium Operations used Tek-Vac Inc. as a reliable small vendor with a proprietary process to clean, electro-polish, and passivate for hydrogen exposure vacuum and other stainless steel fittings and bottles. These parts have provided highly stabilized surfaces enabling analytical measurements using mass spectrometers as well as providing vessels for long term storage of tritium standards. Due to retirement and skill set transitions at Tek-Vac, alternative passivation companies need to be developed. The sources of the steels used by Tek-Vac and others have also changed over time and may have increased levels of hydrogen trapped in the materials.

The following milestones were developed for the past year. Based on observations with the current aluminum housing in our laboratory the purchase of an aluminum expansion volume for Tritium Laboratories was canceled pending further research.

**Table 1: Milestones for PDRD 2015-2016**

<i>Milestone</i>	<i>Start</i>	<i>Complete</i>
<i>Conduct off-gassing calculations and studies</i>	<i>10-1</i>	<i>12-31</i>
<i>Place PO for Al 3L Expansion Chamber</i>	<i>10-1</i>	<i>canceled</i>
<i>Place PO for Cr plating</i>	<i>10-1</i>	<i>12-31</i>
<i>Receive Al Chamber</i>	<i>1-1</i>	<i>canceled</i>
<i>Test Cr plated objects</i>	<i>1-1</i>	<i>3-31</i>
<i>Test Nano-Diamond materials</i>	<i>2-1</i>	<i>3-31</i>
<i>Test Electro-Plated materials</i>	<i>1-1</i>	<i>9-30</i>
<i>Test Cr and Al coated objects</i>	<i>10-1</i>	<i>6-30</i>
<i>Develop LIBS as quick test for surface depth profile</i>	<i>11-1</i>	<i>11-30</i>

### Background

The stability of standards of tritium (T) and deuterium (D) are often problematic due to residual hydrogen that off gases out of the storage vessel walls, possible exchange of D and T with available protium that might be chemical or physical adsorbed and surface interaction with



surface exposed carbides or nitrides. As summarized by Ishikawa and Nemanic a typical Type 304L austenitic stainless steel vacuum surface will have an apparent off gassing rate of around  $5 \times 10^{-12}$  mbar l/s  $\text{cm}^2$  at room temperature. Most of the off gas is hydrogen. Oxidative thermal treatment of the steel can lower the rate several orders of magnitude.<sup>1</sup>

The off gas rate does not measure exchange reactions with bound protium such as from O-H, N-H, and C-H bonds on the surface. It will measure the diffused hydrogen in solution in the stainless steel that permeates from the trapping sites within the metal. An equivalent total off gas rate for stainless steel might be around  $5 \times 10^{-11}$  mbar l/s  $\text{cm}^2$  which is close to the maximum allowable value if there is a 1 percent change in the standard composition permitted in a year. This rate,  $5 \times 10^{-11}$  mbar l/s  $\text{cm}^2$ , shortens the lifetime of a tritium or deuterium standard to less than a year of practical shelf life. In practice tritium standards are often below ambient further limits the acceptable off gassing rate. The lower pressure will cause the standard gas to be more readily contaminated at measurable values by the residual gases, especially protium. Therefore, additional treatments are required to decrease and suppress the background off gas rates so the desired shelf life of several years can be achieved. These same treatments could lead to materials for use in ultra-high vacuum systems.

Treatment of austenitic steels for tritium storage has long been studied and evaluated by those making tritium standards or for those interested in achieving ultra-high vacuum. John Gill at Mound and Elliot Clark at Savannah River have both studied the problem and made comparisons of vessel treatments.<sup>2,3</sup> This work is a continuation and expansion of their studies. The standard treatments are often held as proprietary process but basically involve several steps. These include a cleaning/degreasing washing, a step to polish the surface, a heat step to release the residual hydrogen trapped in the metal from original casting and forming processes, and finally a step to create a permeation barrier that is less permeable to hydrogen than untreated surfaces. All of these steps have supporting research studies. Tito Sasaki has summarized common treatments and in a follow up paper given a recommended cleaning procedures for ultra-high vacuum materials.<sup>4,5</sup>

Courdace, Warwick, and Kim used thermal analysis methods to infer tritium speciation found in metals from nuclear sites.<sup>6</sup> Their study indicated that tritium was bound in three forms. Tritium was loosely bound in water and organics on the surface. Tritium was chemically bound as a hydroxide,  $\text{O}^3\text{H}$  in the surface layers, and tritium was deeply bound in the metal matrix from possible activation products. One can easily infer that protium or deuterium could be bound as a hydroxide or trap in the matrix during metal formation or extrusion. The study showed that surface cleaning and an initial  $100^\circ\text{C}$  bake out would remove the surface contaminants and start to release some of the waters of hydration. One of their studies indicated that aluminum oxide trihydrate transitions to aluminum oxide monohydrate around  $100^\circ\text{C}$ . Further heating indicated that hydroxides transition to the oxide form around  $350^\circ$  releasing hydrogen or in their case

tritium, and that it took temperatures up to 800° C to fully release the deeply bound tritium. The latter requires diffusion of the tritium trapped at binding sites and trapping sites in the metal. It may entail bulk or grain boundary diffusion.

A series of papers by Stupnik and Leish showed the benefit of electro-polishing stainless steel.<sup>7-9</sup> Polishing the surface of the metal not only decreased the available surface area but their work using surface analysis methods suggested that hydrogen would permeate out of a surface easier at the edges than along the exposed planar face; this result can be ascribed to the multi-step process associated with permeation. Hydrogen atoms diffuse through the metal matrix, are exposed to the free surface, recombine to form H<sub>2</sub> molecules and desorb. The hydrogen atoms can more readily reach the free surface of specific crystallographic planes and then subsequently recombine. Polishing the surface removes the number of steps and reduced the hydrogen permeation.

The benefits of thermal treatments are well known to most vacuum scientists. However, these thermal treatments are often highly variable in temperature and duration. Nuvolone studied the degassing rates of 316 L stainless steel by heat treatment.<sup>10</sup> His study indicated that temperatures which would boil off surface water and most hydrocarbons were generally inadequate for significant lowering of residual hydrogen off gas rates. Moderate bake out at 150° C is adequate for re-cleaning of materials that had a prior deep degassing vacuum heat treatment at temperatures between 300° to 400°C. He suggests that an alternative low pressure oxidative treatment at 400°C might also be beneficial. A similar study was reported by Wild who found the heating above 500°C could cause trace sulfur in the steel to migrate and would attack / weaken the surface oxide layers. He also found that higher temperatures would release manganese.<sup>11</sup>

There have been many studies of the permeation of hydrogen isotopes and other gases into metal surfaces relative to temperature and pressure. Most studies show that permeation increases with temperature according to an Arrhenius type of equation. That is a plot of the log of permeation versus the reciprocal of the temperature gives a linear line plot with a negative slope. The permeation of hydrogen due to the gas pressure is not as simple. At normal pressures permeation of hydrogen will tend to be consistent with Sievert's law and is proportional to the square root of the pressure, but at very low pressures often this relationship breaks down. The surface oxidation layer changes the permeation and permeation may be a function of the diatomic gas such as occurs with a molecular sieve or via a mono-atomic hydrogen transfer such as occurs with a metal hydride like palladium. Surfaces where the oxide layer has been removed are more permeable than those with a significant oxide layer. [Strehlow and Savage; Smithells and Ransley; Grant, Cummings and Blackburn; and Steward].<sup>12-15</sup> The relative permeation of protium, deuterium, and tritium follows the reciprocal of the square root of the mass as assumed in Fick's law, but the permeation may change from diatomic molecules to mono atomic ions

depending on the surface exchange reaction. Metals like chromium and aluminum favor the oxide form rather than hydroxide form and tend to block permeation more than species like iron.

Papers by E.H. Van Deventer et al; K. S. Forcey et al.; a review by Hollenberg et al suggest that an aluminum barrier would decrease hydrogen permeation.<sup>16-19</sup> A study by Song, Du, Xu, Long found that aluminum oxide is the actual barrier and that anodized aluminum was less effective than oxides made by heating.<sup>20</sup> Earwaker et al. suggested that Fercalloy heated to 600°C created an aluminum oxide barrier which resulted in up to four orders of magnitude lower permeation of hydrogen compared to iron.<sup>21</sup> Hollenberg et al. charted the equilibrium of hydrogen/water with iron, chromium, and aluminum metal/oxide. Those equations indicate that iron is more likely to exist as a hydroxide than either chromium or aluminum. Therefore decreasing the iron on the surface should decrease the amount of protium exchange. Ozeki et al. reported chromium oxides provide a similar reduction in available hydroxide compared to iron.<sup>22</sup>

Our study compares the application of aluminum and chromium based coatings to act as a barrier to hydrogen permeation. In addition we explored a new nano-diamond coating whose permeation barrier was unknown. The details of the nano-diamond studies led by Dien Li are covered in a separate technical report.<sup>23</sup> Several recent reports suggests nano-diamond might be a viable material for stability in a radiolytic environment.<sup>24-27</sup> Aluminide and chromide coatings were obtained from a commercial supplier using a packed bed coating process. Another coating tested was thin-dense electro-plated chromium. We compare the results to a commercial ultra-clean electro-polished steel canister and to an assembled all aluminum test vessel similar to those used for the coating studies. Residual gas measurements using a mass spectrometer were followed with vacuum bake out treatments monitored with a residual gas mass analyzer. Deuterium was used as the primary load gas for the test measurements.

A new testing method was developed for evaluating stability of a deuterium standard. Vessels were loaded to one thousandth of a standard loading. For example a 100 ml volume container was loaded to 760 mTorr instead of the usual 760 Torr. This is equivalent to loading 100 microliters of gas at STP. Outgassing of just a few microliters from the vessel walls was easily detected as corruption of the deuterium mix in just a couple of weeks of storage. In contrast the study done by Clark in our laboratory used vessels in storage up to two years. Clark studies had shown that most of CT<sub>4</sub> and H<sub>2</sub> occurred due to the initial residual outgassing.<sup>28-30</sup>

## **2.0 Experimental Procedure**

### **2.1 Aluminizing and Chromizing**

Five hundred (500) ml Swagelok cylinders were aluminized by Praxair Surface Technology, Biddeford, ME using a proprietary pack aluminizing process. The threads on the bottles and

plugs were masked with a paint-on maskant to preclude coating. The parts were pack aluminized using Praxair standard SDC-1573 powder and furnace cycle. The bottles were diffused at a temperature between 705 and 760°C for two hours in a hydrogen atmosphere. Sample coupons were coated simultaneously for coating thickness and composition measurement.

Five hundred (500) ml Swagelok cylinders were chromized by Praxair Surface Technology, Biddeford, ME using a proprietary pack chromizing process. The threads on the bottles and plugs were masked with a paint-on maskant to preclude coating. The parts were pack chromized using the Praxair standard chromizing run at 843°C for the standard time in a hydrogen atmosphere. Sample coupons were coated simultaneously for coating thickness and composition measurement.

## 2.2 Chrome Plating

ConFlat(TM) pipe nipples, blank flanges and VCR to CF adapters were plated with a proprietary thin dense chromium layer, ARMTEC, by Meadville plating. ARMTEC thin dense chrome is applied electrolytically, resulting in a bond superior to plating or coatings applied without the use of electricity (e.g., electroless nickel, etc.). The chromium coatings from this process are satin in appearance and have a thickness typically of 1.3  $\mu\text{m}$ .

## 2.3 Plating processes for ND coatings

The ND coating was comprised of three main material components plated by Engis Corporation, Wheeling, IL. The first was a Wood's nickel. It was plated in a Wood's nickel strike type plating bath and was used as a base layer to promote adhesion of copper to stainless steel materials. The bath make-up was low nickel metal and high acid content. The second component was an electroless copper. In this plating, Accu-Labs 855 Electroless Copper plating process was used. The solution is a mixture of two proprietary components, 855-M and 855-A, as well as small percentages of liquid caustic soda (50% High Purity) and formaldehyde (37% High Purity) in deionized (DI) water. Another proprietary component, 855-R acts as a replenishment to replace chemistry lost throughout the plating process. The third component was nano-diamond (ND). A 65 nm ND used in this project was acid cleaned, and suspended in the copper plating solution to create the copper-ND composite coating. The elemental impurities of this ND were analyzed using Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP-OES), and its particle size distribution (PSD) was analyzed using CPS Disc Centrifuge Nano Particle Size Analyzer.

## 2.4 SEM and EDX Characterization

The scanning electron microscope (SEM) used in this project was a Hitachi S3600N with an Oxford Instruments INCA Energy for Energy dispersive X-ray (EDX) spectroscopy. Various components were examined by SEM-EDX. Typically, the SEM images were captured after optimizing the experimental parameters (e.g., working distance, accelerating voltage and magnification) within the limits of this SEM instrument. For EDX, the spectra were collected

using a voltage of 0-10 keV, optimal working distance of 15 mm, data acquisition time of 55 seconds. Mapping was also performed until adequate elemental maps were constructed.

### 2.5 Test Vessels:

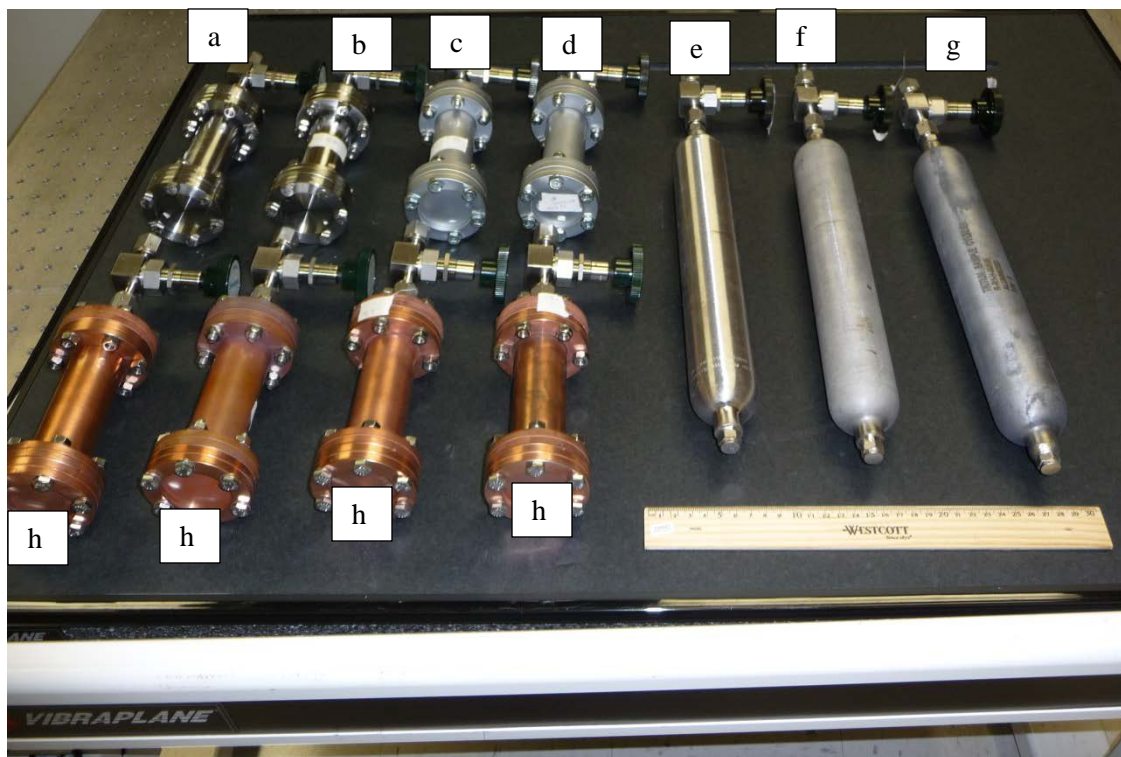
Test vessels were constructed to hold a nominal 100 milliliter internal volume and called ConFlat Vessel Assembly (CFVA). The vessels started with a standard 304L 125 mm 275-150-N nipple with 2.75" ConFlat(TM) end fittings and a 1.5" tube diameter. The CFVA had a 2.75" end cap on one end and a 2.75" end cap to male VCR-4 adapter on the other. The VCR-4 adapter was coupled to a Swagelok electropolished and cleaned SS-4BG bellows valve as shown in figure 1. The vessels were treated or coated for the tests. Coatings included:

- copper,
- copper with 25% nano-diamond
- copper with 50% nano-diamond
- unpolished "as received" Stainless Steel 304L
- electro-polished SS 304L
- dense Cr plate
- dense Cr plate with electro-polish cleaning

An alternative CFVA was made in aluminum 6061 with aluminum endcaps. A few gas sample bottles were constructed from Swagelok 304L-HD5-500 500 mL tubes with welded endcaps. These gas sample bottles had chromized, aluminized, and 304L surfaces. In addition commercial 400 mL low pressure gas sampling canisters were obtained from Restek Corporation. Two types of Restek gas sampling canisters were tested, either electro-polished stainless steel or Siltek treated. The Restek electro-polished canister became the reference standard for this work.

The internal surfaces of CFVA were coated with Cu, 25%, or 50% ND-Cu for surface passivation purpose, as previously described, while the external surfaces of the copper – ND parts were coated with plain Cu for decoration purposes. Similar CFVA were prepared from as received parts, electro-polished steel, chrome plated steel, chrome plated and electropolished chrome plate.

Two CFVA were made from aluminum vacuum fittings obtained from W.L. Schoonover, Canton, GA. Aluminum vacuum parts with equivalent geometry to the steel ones were made using Al 6061 aluminum. One of the aluminum CFVA was sealed with aluminum gaskets. The other used copper gasket for seals. Copper gaskets were used in the other 100 mL test CFVA.



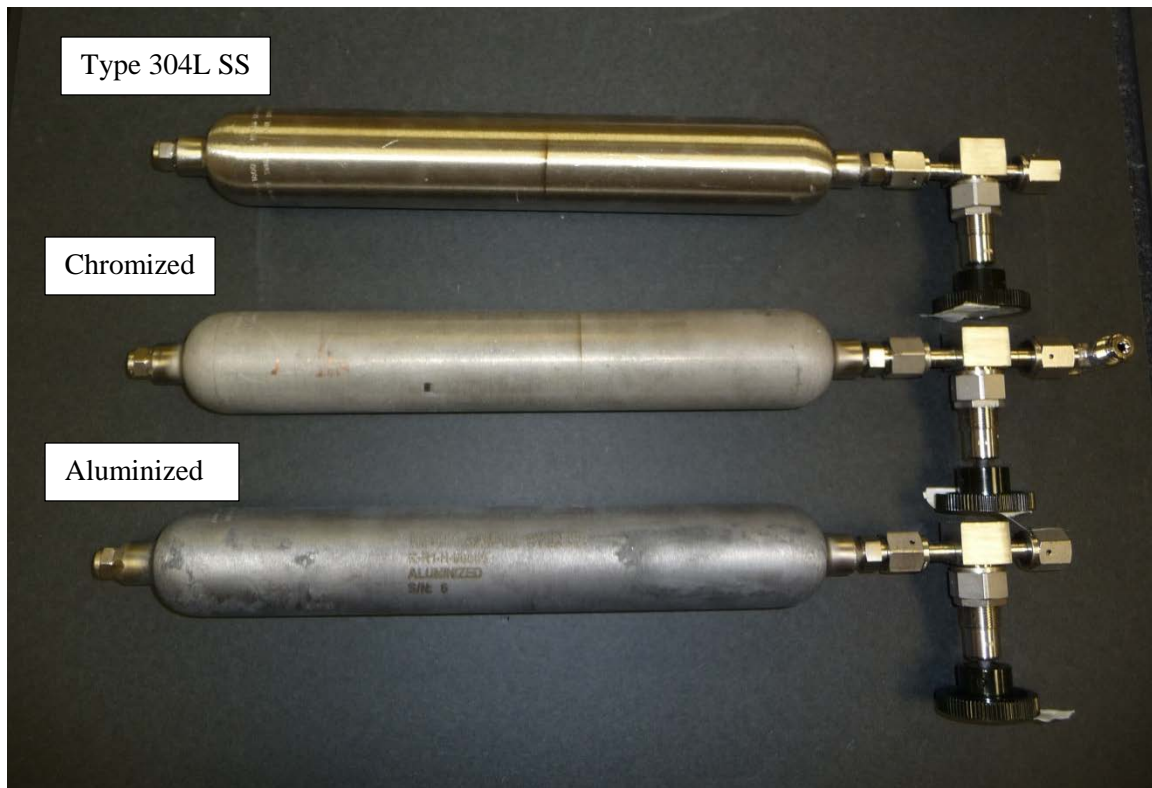
**Figure 2** Photograph of Gas Bottle Assemblies (a) Type 304L SS (b) Type 304L SS Commercially EP (c) Cr plated Type 304L SS (d) Cr plated Type 304L SS Commercially EP (e) Swagelok 500 ml Type 304L bottle, (f) Chromized Swagelok 500 ml Type 304L bottle, (g) aluminized Swagelok 500 ml Type 304L bottle, (h) electroless plated Cu or Cu-ND on Type 304L SS

Before loading deuterium, the 500 mL bottles were placed on the inlet manifold and evacuated and baked out at 120°C using heating tape. The CFVAs were not baked out but evacuated as received. All vessels were checked for air leakage when connected. Selected bottles were retested if air leakage or after going thru an extended vacuum bake out as discussed below. Gas bottles were checked for leaks to  $<1 \times 10^{-9}$  cc/s at 21°C [room temperature] or the limit of the monitoring mass spectrometer.



**Figure 3 100 mL vessels with copper, nano-diamond, chrome, and steel treatments**





**Figure 4 External surface appearance of Praxair aluminized and chromized coatings compared to standard Type 304L SS gas sample bottles.**

## 2.6 Mass Spectrometry Experimental Test Procedure:

The standard testing of the vessels was to evacuate and conduct a simple rate of rise to check for gross leakage. The vessels were loaded with approximately a thousandth of an atmosphere with deuterium and then changes in the deuterium and residual ions were monitored with periodic sampling to a quadrupole mass spectrometer. For a 100 mL volume this amounted to watching the impurity growth in the initial 100 microliter load at 1 mbar compared to a typical load of a 100 mL at 1000 mbar. Testing extended over several months. Vessels were evacuated and checked for leaks to  $<1\text{E-}9$  cc/s at STP or the limit of the monitoring mass spectrometer. After leak testing deuterium was loaded using a custom built manifold system that had been used for 50 years at Savannah River to load vessels for in-house gas leak standards. Pressure was measured with 10 Torr and 1 Torr MKS Baratron gauges and lines were evacuated with a 300L/min Turbo vacuum system. The loading was under computer pneumatic valve control using a FESTO controller. Deuterium gas was  $>99.8\%$   $\text{D}_2$  with traces of HD and  $\text{H}_2$ , which likely came from hydrogen outgassing within the storage vessel.



The mass spectrometer was a 400-5 series Pfeiffer quadrupole with a large HiPACE 400 turbo pump backed with a secondary turbo pump station. The spectrometer ran the Inficon Quadera software package and normally set to scan to mass 65 using the secondary electron multiplier (SecEM) detector with 1500V gain. These settings allowed the system to detect impurities at ppm level in atmospheric pressure samples for most gases of interest. A 0.1% change in test samples was easily observed and equivalent to 1 ppm for nitrogen or carbon monoxide at atmospheric pressure. Sensitivity for hydrogen was approximately twice that of nitrogen in this spectrometer but deuterium was equivalent to nitrogen. Mass resolution was set for 0.5 amu. The system was set to continuously scan and store data during measurements. Spectrometer pressure was measured using a Pfeiffer PB-260 full range gauge with a hot cathode. Post processing of the data with Excel allowed concentrations to be extrapolated to load zero time and account for pumping diffusion rate. System background was limited by the rhenium filaments in use. The filaments emitted oxygen, rhenium<sup>++</sup>, and rhenium<sup>+</sup> ions as well as several trace hydrocarbon and alkali impurities depending on the filament batch. Hydrogen, water, carbon monoxide, and carbon dioxide were also in background spectra and varied over time. The spectrometer was mounted in aluminum housing for vacuum containment which helped lower system hydrogen and water background. A small SAES D100 ion getter pump assisted pumping of hydrogen.

Actual measurements were made by expanding a sample aliquot from the test vessel to give deuterium about  $2\text{E-}7$  mbar reading on the spectrometer pressure gauge. Typical ion currents ran from  $5\text{E-}7$  amps to  $2\text{E-}13$  amps, which were the sample deuterium peak current and the electronic noise floor for the SecEM detector being used. Individual ion backgrounds increased the instrumentation limit for several ion lines and background was somewhat pressure dependent.

All data was normalized to the deuterium spectra at 1 mbar pressure. The deuterium reference signal which included the residual background signal was then subtracted from each vessel data set. The background level from a new deuterium aliquot was used to correct sample measurements for system background.

The sample load on the mass spectrometer was kept low at about  $2\text{E-}7$  mbar pressure which limited the pressure dependent formation of  $\text{D}_3^+$ ,  $\text{H}_3^+$ ,  $\text{HD}_2^+$ , and  $\text{D}_2\text{H}^+$  within the ion source. Sample pressure to achieve ultra-trace measurements could be raised to  $1\text{E-}5$  mbar with some added protonation or deuteration observed in the spectra.

## 2.7 Tube Furnace for Vacuum Baking

A tube furnace system was assembled in-house from commercially available vacuum furnace components, 4 inch diameter pipe nipples with 6 inch ConFlat flanges. The hardware included Temperature Controllers - Digi Sense 68900-11, Over Temperature Controllers - Over-Temp Probe OTP-1800, vacuum - Pfeiffer HiCube 80 Eco, Pressure Gauge - Pfeiffer Dual Gauge TPG 362, and RGA - AMETEK Dycor Dymaxion Residual Gas Analyzer. The software included Temperature/Vacuum Pressure monitoring - Labview 15.0, and RGA monitoring - Dycor System 2000. The heater control system is pressure-dependent, and a Labview program was developed to control the temp controllers on the vacuum furnace. There is a dead band programmed in the Pfeiffer Dual Gauge to cut off power to the heaters when pressure exceeds  $1.0 \times 10^{-6}$  Torr and not restore power until pressures drop below  $9 \times 10^{-7}$  Torr. This furnace system was used to extract intrinsic hydrogen entrapped in the baseline stainless steel CFVA components, the aluminized, chromized, chromium plated, Cu, Cu-ND coated samples. After loading and prior to heating, vacuum pressure was allowed to pull down to  $<4.0 \times 10^{-8}$  Torr. The samples were evacuated at room temperature for 12 to 24 hours to achieve this vacuum level. The samples were heated such that the pressure did not exceed  $1.8 \times 10^{-6}$  Torr. The vacuum extraction process was stopped after the pressure reached the low to mid  $10^{-8}$  Torr. The samples were removed after the furnace chamber cooled to below  $35^\circ\text{C}$ .

## 2.8 LIBS Measurements

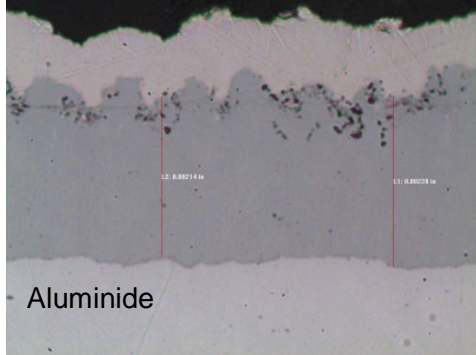
Laser Induced Breakdown Spectroscopy (LIBS) was used to evaluate treatments of stainless steel coupons. However the system was also used to check vessel coatings. The LIBS system was assembled in-house using a CETAC LSX-200 laser ablation system with a Big Sky Ultra laser set for 266 nm laser emission with an 8 nanosecond pulse at 4 micro joules. Emission was detected using a fiber optic coupled Andor Mechelle spectrograph with an Andor ICCD 734 series camera. The standard analysis used a 200 micron laser spot size (#6) with a 1 microsecond delay and 100 microsecond capture gate window. The spectrometer captured emissions from 250-920 nm. Coupon samples were purged in argon but larger pieces required analysis in air.

## **3.0 Results and Discussion**

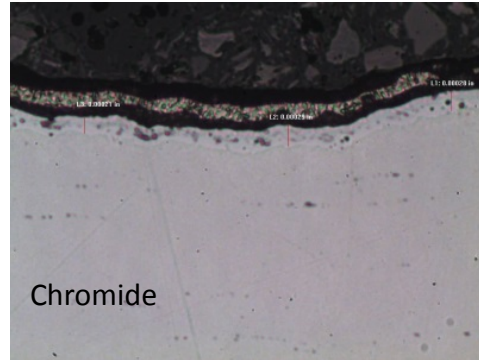
### 3.1 Coating Characterization

One of the acceptance requirements for the aluminide and chromide coatings was that the vendor performs coating thickness measurements, microstructure analysis, and composition. Sacrificial sample

coupons were coated in parallel with the gas bottles. These were prepared for optical and scanning electron microscopy. The coating thickness was measured using the optical microstructure images. These are shown in Figures 5 and 6. The aluminide coating was, on average, 50  $\mu\text{m}$  thick and the chromide coating was 6  $\mu\text{m}$ , on average. In contrast a typical clean electro-polished 304L has between 0.7 to 4 nm chromium oxide layer according to Auger measurements in our lab<sup>28-30</sup>.



**Figure 5 Aluminide layer**



**Figure 6 Chromide layer**

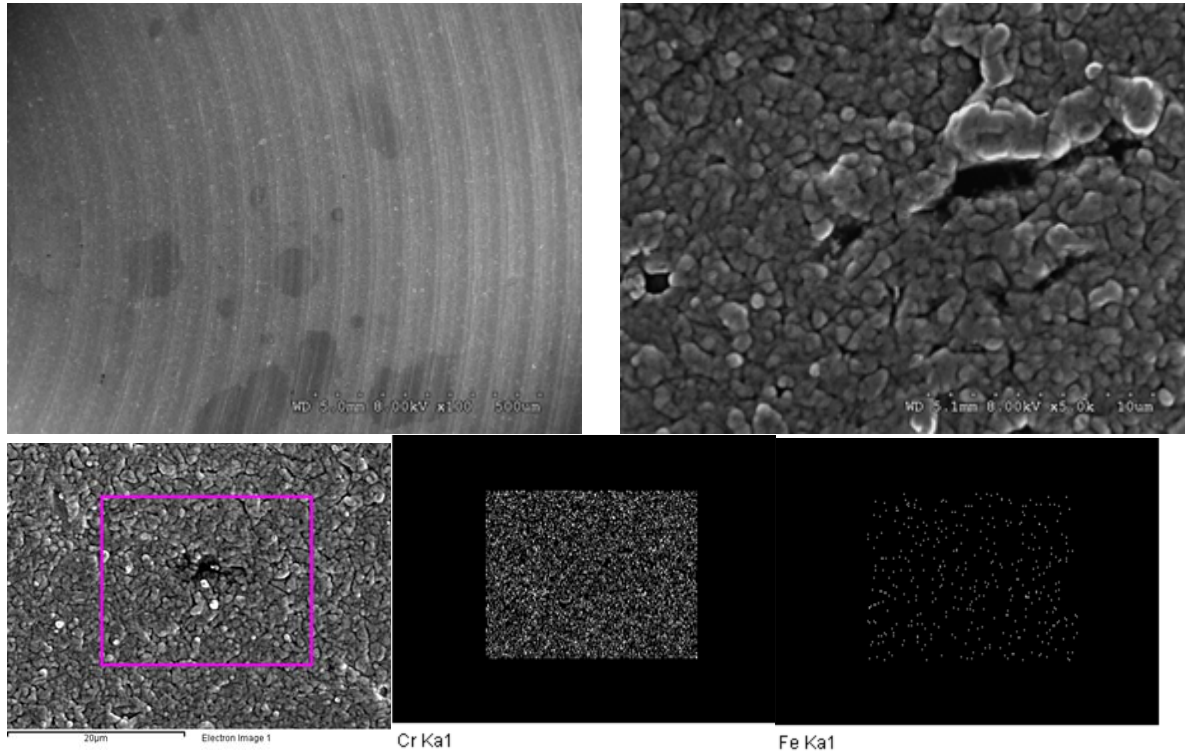
The coating composition was measured using SEM and EDS. The aluminide coating appears to be single phase iron aluminide with a very small inter-diffusion layer and a few oxides and pores in the outer region of the coating. The coating is very high in Al with content in excess of 50%; the nominal coating composition of the aluminide coating is listed in Table 2. The chromide coating was similarly evaluated and this coating exhibits a few pores directly below the chromide coating and a small inter-diffusion layer, Figure 6. The coating is over 97% Cr, as listed in Table 2.

**Table 2 Coating composition in percent for aluminide and chromide coatings**

Coating	Al	Fe	Cr	Ni	Mn	Co
Aluminide	54.1	32.7	8.4	3.9	0.7	0.2
Chromide		1.0	97.3	1.7		

The copper nano-diamond coatings were also characterized and the details for these CFVA are presented in Li et al<sup>23</sup>.

The chromium plated samples were examined using SEM and EDS as well. The typical surface appearance of the Cr plated CF blank is shown in Figure 7. The EDS data is shown in Figure 8. It is apparent that the coating conforms well to the machined surface grooves. There are no large gaps in the coating. The coating exhibits fairly fine crystallites on the surface with a few coating defects. EDS chemical analysis revealed Cr and C only. The coating was not examined in cross-section and the coating



**Figure 7 Surface appearance of the Cr plated CF blank flange at low and high magnification. The coating holiday does not appear to extend through the thickness based on the lack of Fe signal in the EDS X-ray map.**

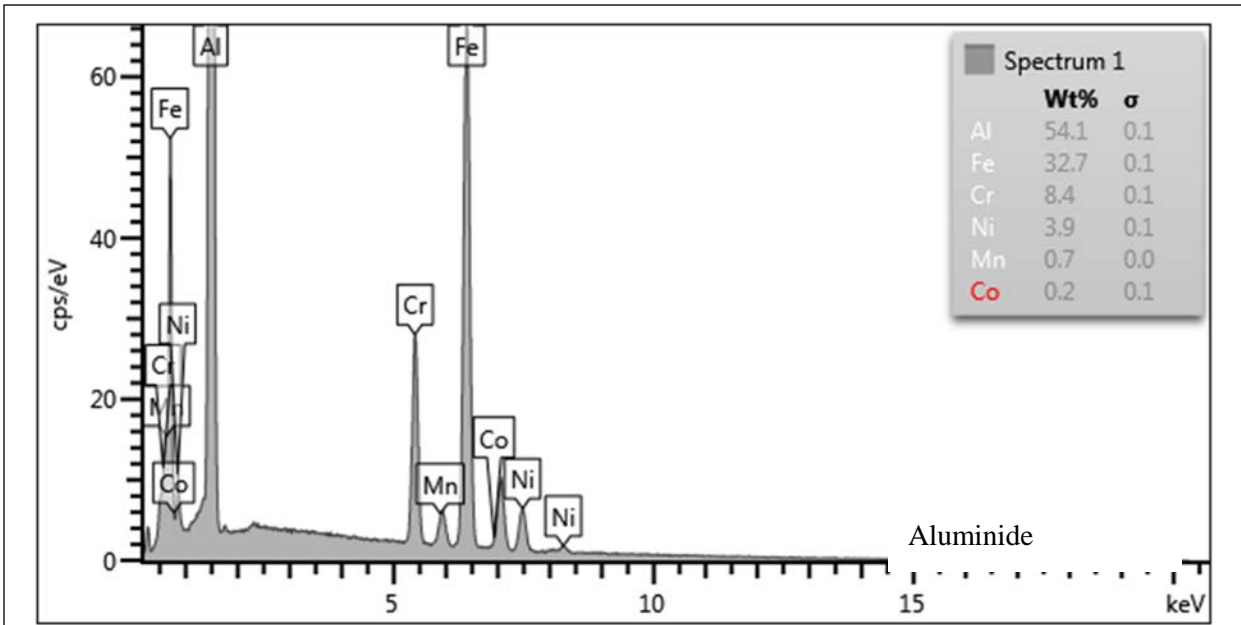


Figure 8 EDS of aluminide coating.

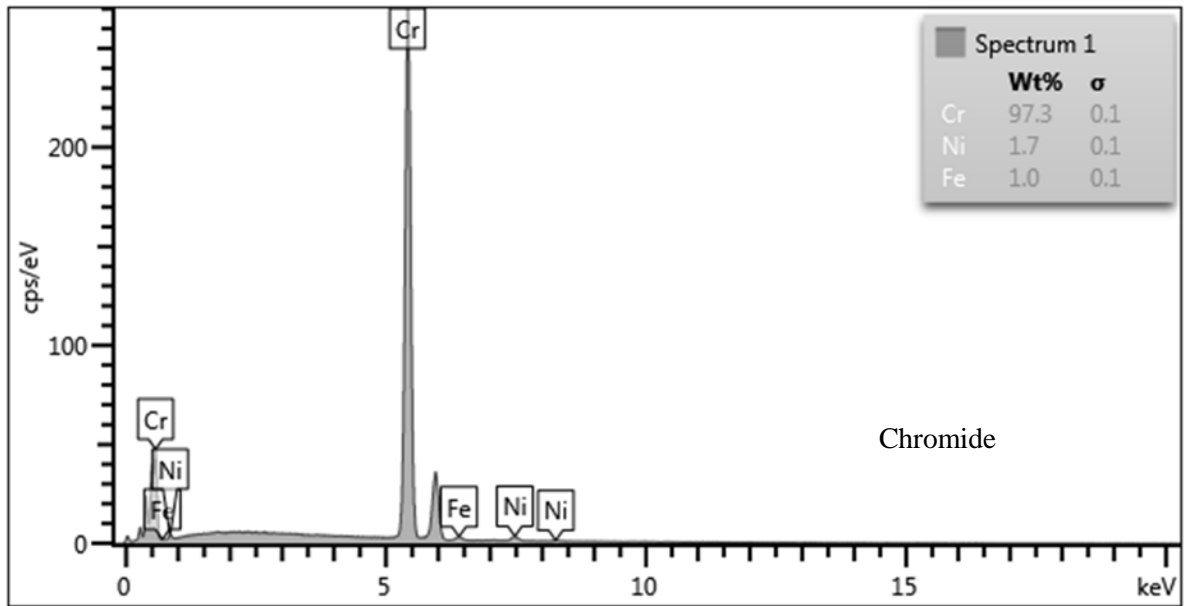


Figure 9 EDS of chromide coating.

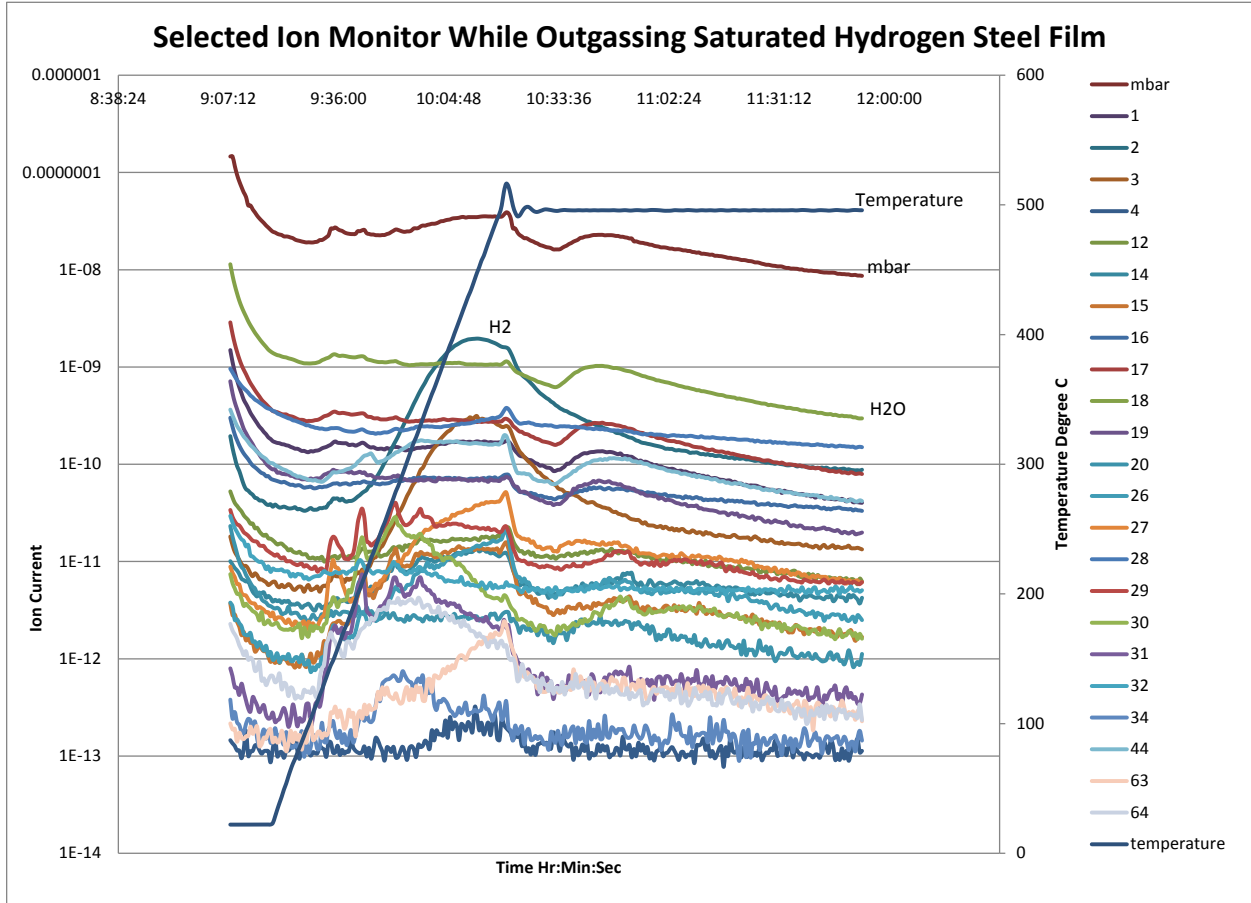
Several vessels were qualitatively tested with a LIBS spectrometer that indicated the surface profile as well as detected most of the elemental components. The LIBS system poorly detected carbon, sulfur, and phosphorous. The chromized coating had substantial alkali metals in addition to chromium. EDS does readily detect lithium. Na, Li, and some K were in the outer layers of the chromide coatings. The amount increased with the first couple of laser pulses but then depleted with penetration depth. Each laser pulse penetrated about 200 nm. The 304L steel samples indicated mostly chromium and some iron at the surface with nickel appearing after penetration of the surface. Cleaned and polished steel samples had an initial smaller surface signal indicating significant oxide coating. Chromium and then iron, manganese, and nickel increased with depth. Dirty and unpolished steel had sodium and potassium on the surface and often a significant amount of chromium that readily dropped away with penetration depth. Calcium and aluminum were sometimes detected in the initial pulse and thought to be surface dust from insulation materials. The LIBS system could readily detect samples that had been handled with bare hands as body salts were readily detected. Unlike the chromized plated sample sodium and potassium were low values in clean steel samples. The aluminum sample indicated aluminum and some magnesium as expected for AL6061. Our LIBS spectrometer could not detect the nano-diamond carbon but readily detected copper as well as sodium in the copper coated surfaces. The LIBS pulse penetration was estimated to be 200 nm/pulse, which was too deep to readily detect the thin chromium enhanced layer on the treated steel sample but was adequate for monitoring the plated samples.

### 3.2 Thermal Evolution of Outgas from 304L Steel

To achieve an initial understanding of the out gassing of 304L steel, a thin sheet of type 304L SS shim stock was placed in a vessel loaded with nominal 1 atm of hydrogen at room temperature, sealed and heated to 500°C, ~2.6 atm H<sub>2</sub>, and held for 12 hours. This treatment saturated the 0.005 inch thick stainless steel with hydrogen and should have resulted in approximately 200 wppm H in the stainless steel. The shim stock was handled normally in the air after cooling.

The H<sub>2</sub> loaded shim stock was placed inside of a thimble (0.5 inch diameter SS closed ended tube) that had been evacuated for 24 hours at 650°C to remove residual hydrogen and connected directly to the mass spectrometer while undergoing a controlled heating profile to 500° C. The evolved gas was monitored. As shown in Figure 10 several distinct features of out gas are observed. Water and some hydrocarbons are observed to outgas below 100°C and continue in spurts up to 150°C. This is followed by some transitions in CO and CO<sub>2</sub> and H<sub>2</sub>O release likely associated with the breakdown and oxidation of hydrocarbons on the surface of the stainless steel and contaminant in the thimble. The release of hydrogen from the Shim becomes noticeable at 200°C and dominates the evolved gas at 350°C while increasing as expected by the permeation rate as temperature increased and then decreasing as the dissolved gas in the shim depleted. Water was still being released or more likely being formed at the surface at the max test temperature of 500°C. We should note that this was a well handled film with noticeable finger prints on it. A secondary run with a cleaner sample tended to show less hydrocarbons

but the hydrogen release was consistent. Hydrogen eventually outgasses at the higher temperatures but outgassing is barely changed at bake-outs below 150° C. In our system outgassing showed a thermal pressure gradient that resulted in a distinct pressure transition when steady state was achieved at 500°C. This gradient could be mitigated by using a slower heating ramp.



**Figure 10 Evolved off gas from stainless steel shim stock that was saturated in 2.5 atm hydrogen at 500°C per selected mass ion.**

### 3.3 Individual tests with deuterium

Individual tests were run on each CFVA and bottle in the as-received condition. The 500 mL aluminized and chromized bottles were assembled and leak checked along with an untreated 304L bottle. Prior to welding the fittings, each bottle was subjected to a 2 hour vacuum heat treatment at 350° C, the bottles were welded and then leak checked. The bottles were placed on the mass spectrometer and off gassing were observed in the blank vessels. The aluminized bottle released water and hydrogen, the chromized bottle evolved hydrogen, and the 304 L vessel evolved small quantities of water and hydrogen. Further testing showed that the 2 hour 350°C vacuum bake out was inadequate to remove the residual hydrogen. After vacuum treatment for multiple days while monitoring the residual off gas in a 450°C vacuum chamber, [vessels estimated to be approximately 350°C], all bottles had similar performance and achieved just adequate leak rates. The chromium CFVA continued to evolve small quantities of hydrogen but exhibited less exchange to form HD than the 304L vessel. The aluminum vessel and the 304L vessel showed little difference in the tests. Both the aluminide and chromide coating added hydrogen to the bottles compared to the starting 304L blank. The aluminized bottle may have picked up some moisture in vendor post cleaning steps or during cooling after the coatings.

All three 500 mL bottles exhibited more outgassing than was observed in two of Ultra-Clean 400 mL gas sampling canisters purchased from Restek with RAVE shutoff valves. One Restek 400 ml gas sample bottles were electro-polished steel and the other was electro-polished with a Siltek coated surface. Both of the Restek bottles performed similarly in the tests and because of their superior performance were used as the standard for off-gas comparison. The off-gas levels were an order of magnitude below those achieved with the Swagelok high pressure stainless steel 500 mL bottles. Further testing with the 500 mL bottles was suspended after these results and additional studies focused on a smaller 100 mL vessels that were easier to coat, seal, bake out, and study.

Additional experiments were conducted using vessels assembled from standard vacuum parts. A 2.75" connection tube was end capped to a blank flange and a flange with a standard quarter inch VCR fitting connected to a Swagelok-4-BG clean and electropolished bellows valve that was known to have minimal off gassing and used in our facilities. As shown in figure 3 we called this ConFlat vessel assembly (CFVA). Copper gaskets were used to form seals. Evaluation of the data from several of the experiments, suggest that the copper gaskets cause a limiting condition for exchange and other behaviors for this type of vessel assembly test and future studies should seek ways to limit their use, perhaps by using plated copper gaskets or other suitably soft materials, or by welding the assembly. The 500 mL bottles did not use gaskets but had fully welded seals. The Restek bottles used gas tungsten arc welded (GTAW) seals that were prepared under sterile and clean room conditions. Similar welding conditions are required in the specifications for a standard CTCV.

Each of the CFVA was loaded with deuterium and then monitored after approximately a week of storage. A few CFVA had to be resealed and reloaded with deuterium due to observed air in-leakage. The longer term storage detected minor in-leakage of air better than the initial leak test and some CFVA required additional seal tightening. These leaks did provide some indication of the effect of oxygen and nitrogen

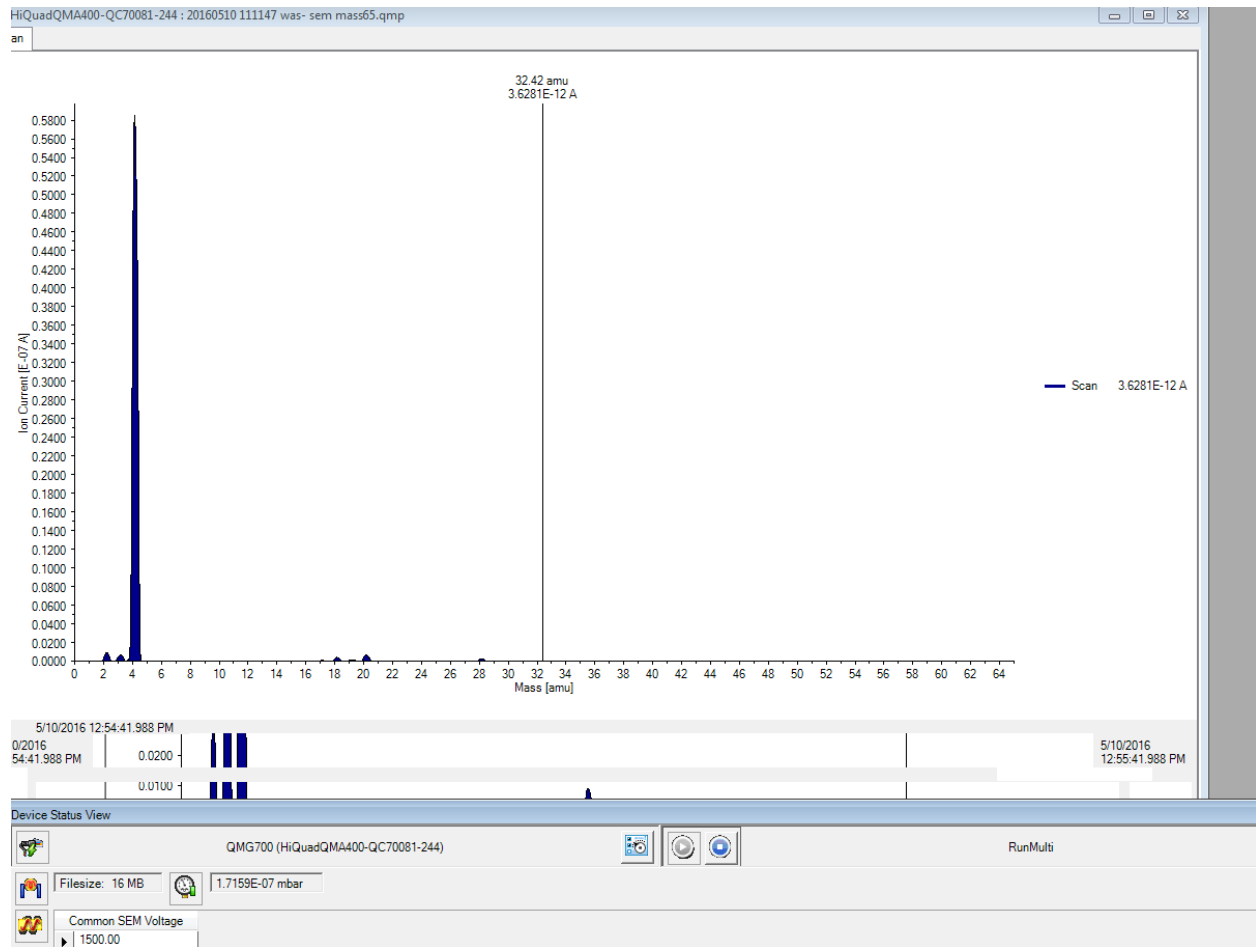


on leak rates. Surprisingly when the air was taken into account, it was found to have little effect on the hydrogen off-gas rate. Because gas was limited in the test vessels, initially at 1 mbar, the opportunity to capture multiple samples was limited as the pressure was reduced with each aliquot to the mass spectrometer. To account for the pressure drop in the CFVA the data sets were normalized and scaled to a constant deuterium level. This normalization introduced some bias in the data since the lower pressure sampling was closer to the residual background. However, the data trends appeared to be consistent.

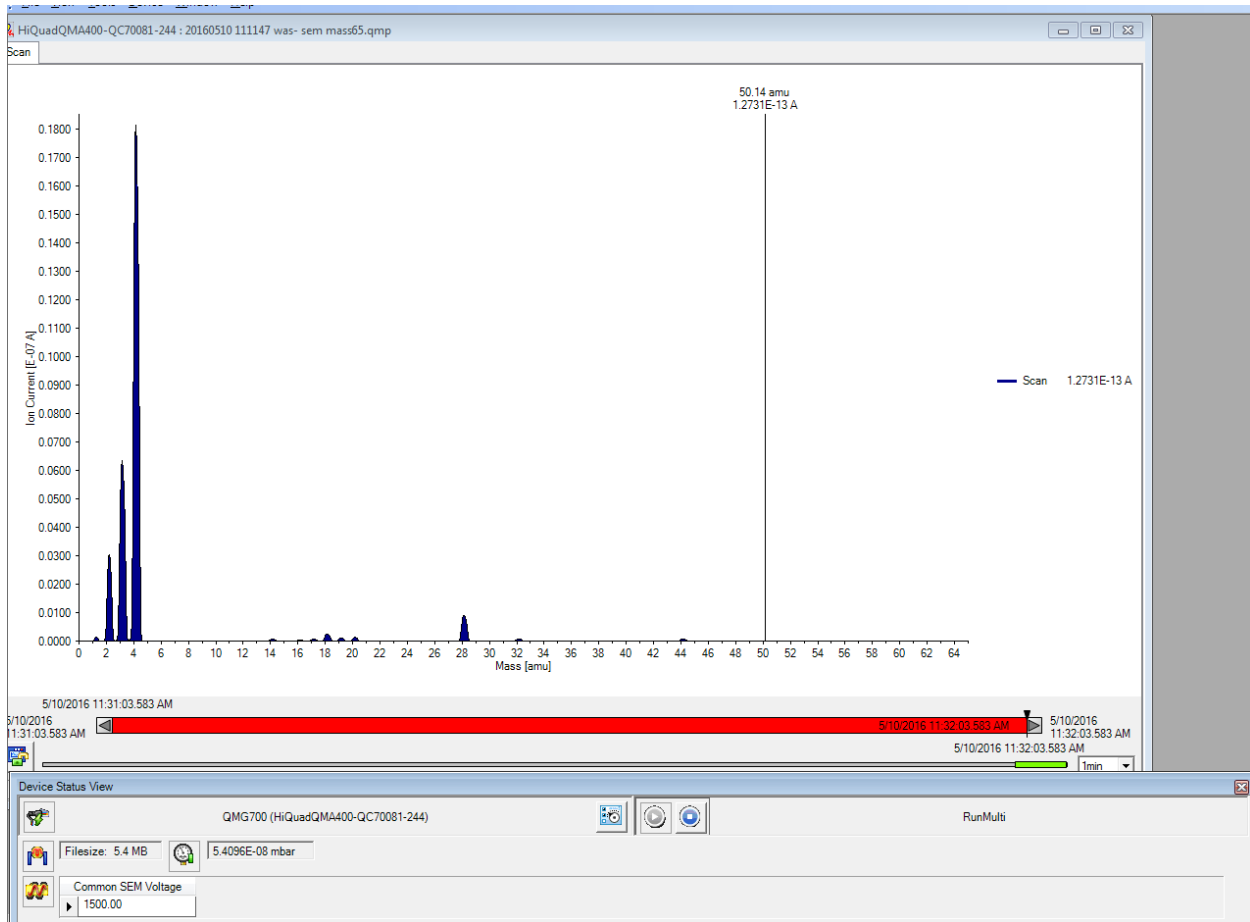
Several CFVA were retested after the initial off-gas tests. The results indicate that CFVA and bottles that were reloaded and those in later retests had lower off gas rates than the first set of CFVA and bottles that were tested. This result was consistent with early work in our laboratory by Elliot Clark<sup>27-28</sup>. Exchange likely takes place on the surface at easily accessible exchange sites and then a much slower exchange or release rate occurs with more deeply embedded or trapped hydrogen. The observation suggests that a tritium standard might be more stable if initially added to a vessel, allowed to stand a few days, unloaded, and then reloaded. The idea would be stabilize or equilibrate the surface with the standard mixture to remove the fast isotope exchanges.

Each of the surfaces tended to have different catalytic effects on the rate of HD formation as well as available water. The relative apparent rate of exchanged appeared to be: Nano-diamond-Cu>Copper>304L>Electro-polished 304L > Aluminum > Chromium. Water appeared to be less in the Al 6061 aluminum CFVA but the aluminide coated bottle required vacuum heating to dry the surfaces and remove adsorbed and possibly chemisorbed water. Stainless steel CFVA tended to retain more water than either the Al 6061 aluminum CFVA or chromium plated CFVA and vacuum extracted electroless copper plated CFVA and vacuum extracted electroless Cu- nano-diamond coated CFVA.

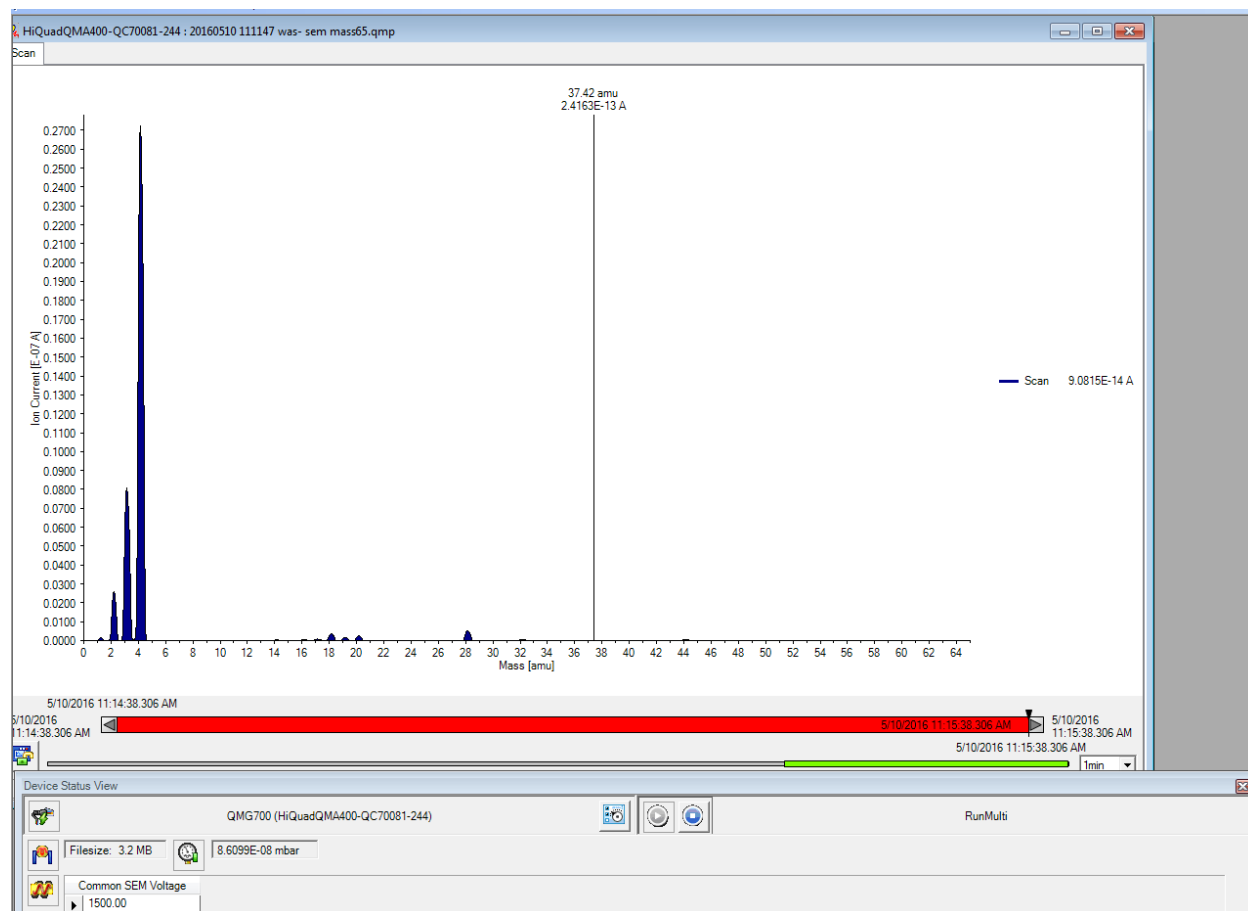
The initial spectra of the first sampling compared to the deuterium standard spectra were informative as shown in Figures 11 to 16. It is worth discussing the spectrum of deuterium using the quadrupole. The main peak for the load is at mass 4 for D<sub>2</sub>. Mass 3 indicates a trace of HD. Mass 2 indicates D<sup>+</sup> and residual H<sub>2</sub>. D<sup>+</sup> is a fragmentation product of D<sub>2</sub>. If we assume that H and D were at equilibrium in the standard and using the HD content at mass 3 as the indicator for H the H<sub>2</sub> would not be visible in the spectra shown. For example at equilibrium at room temperature a mix of 99% D and 1% H would have the mass distribution: .0012 at mass 2, .019 at mass 3, and .970 at mass 4. The spectra seen in the test bottles clearly indicate that hydrogen gas was being added to the gas mix above the initial load and in some cases stayed at mass 2, (H<sub>2</sub>), and in other cases converted in part to mass 3, (HD), indicating that an exchange reaction occurred.



**Figure 11 Deuterium Standard the small signal at mass 2 is D instead of H<sub>2</sub>. A trace HD was observed at mass 3 and residual water and air varied depending on loading day.**



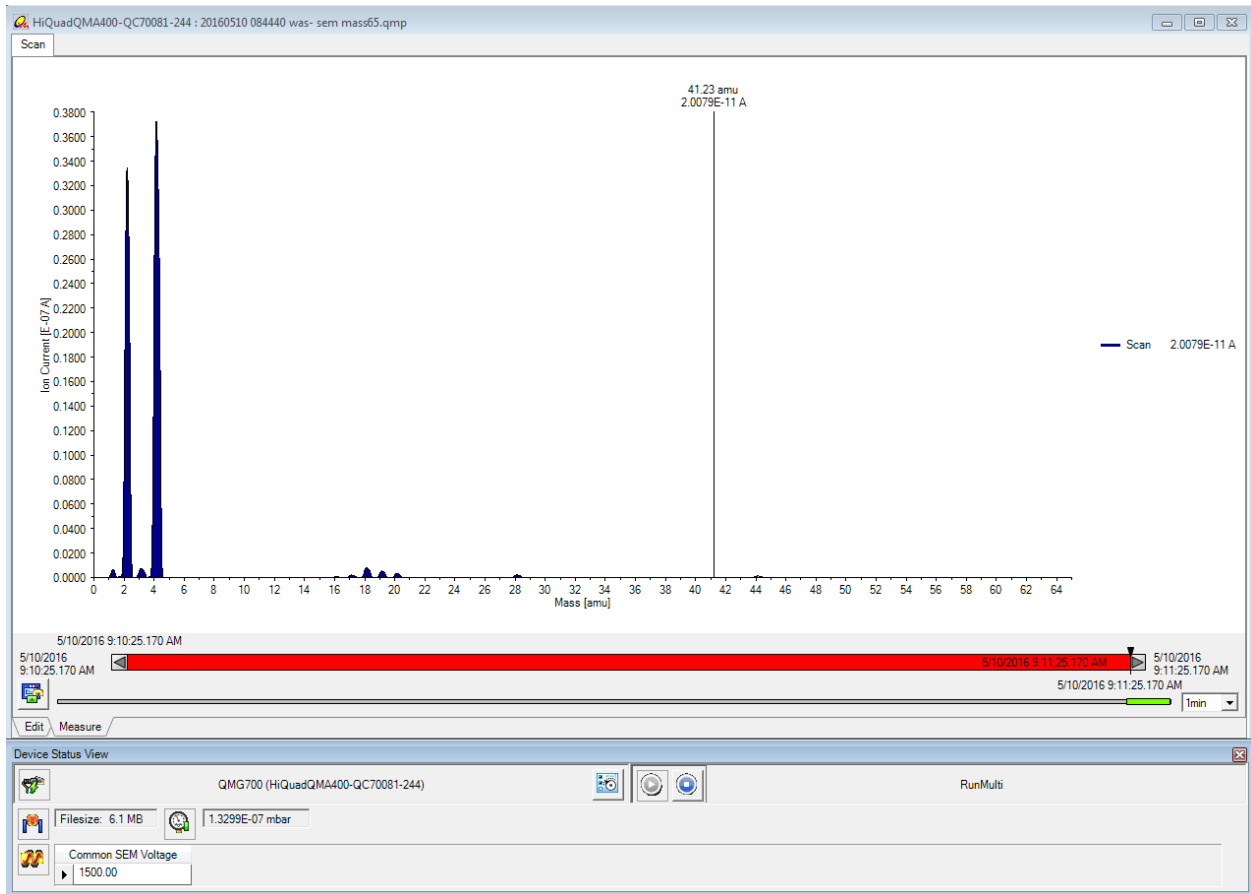
**Figure 12 Spectra of untreated Type 304L stainless steel CFVA had noticeable HD formation and some CO.**



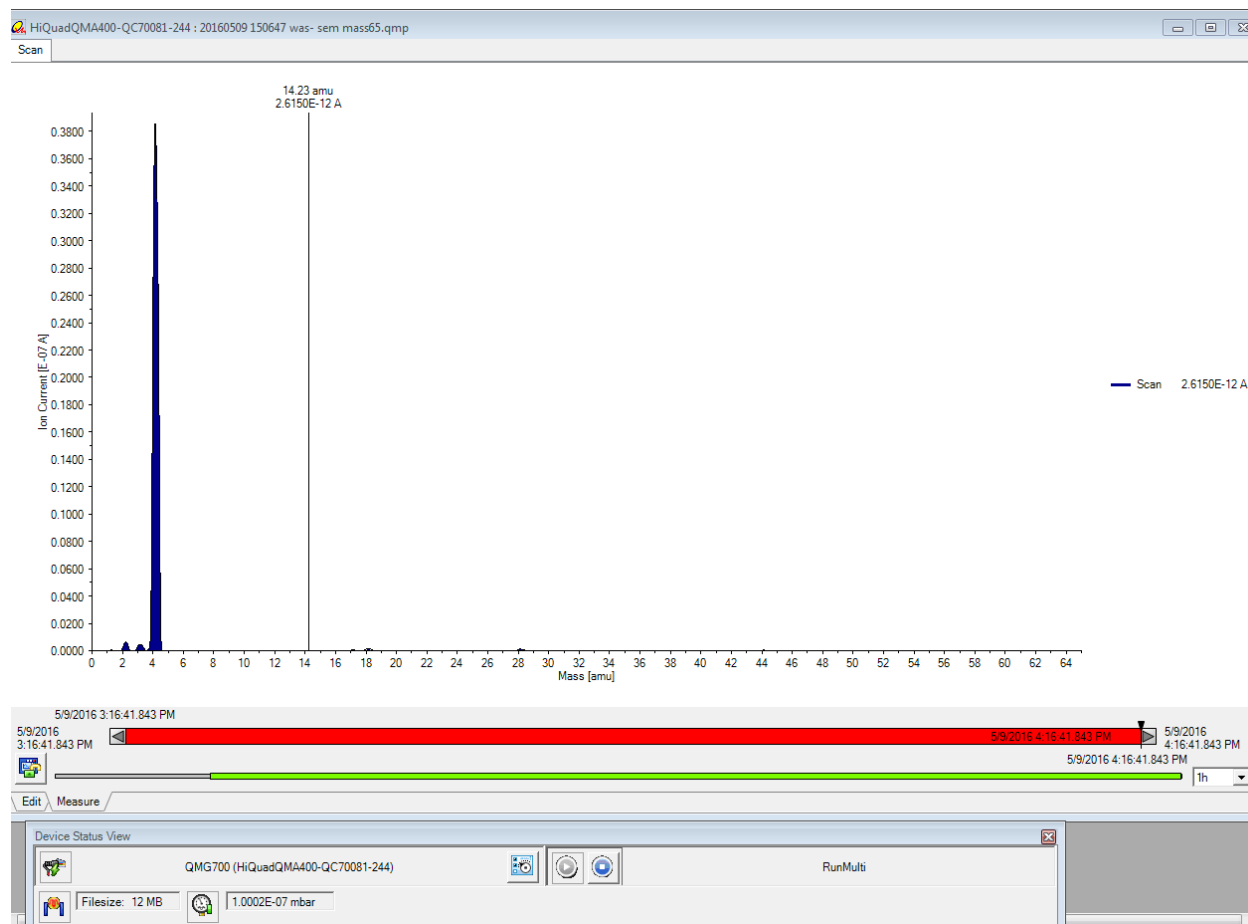
**Figure 13 Electro-polished Type 304L SS CFVA was similar to Type 304L SS but less CO and residuals. HD formation was observed in most of the stainless steel CFVA indicating presence of exchange sites.**



**Figure 14** The Cu-25% ND coated CFVA had so much hydrogen off-gas that the initial deuterium load was minor. HD appeared to be near at equilibrium with the H and D mix. The hydrogen ingrowth was due to the electroless copper ND coating process.



**Figure 15 Electro-plated chrome coated CFVA showed significant hydrogen off gas in the as received condition but exhibited little HD formation. Hydrogen was generated and diffused during coating process.**



**Figure 16** The Restek Electro-polished gas sample bottle contained the deuterium at nearly the same composition as the initial standard. The Siltek gas sample bottle exhibited similar behavior.

### 3.4 Vacuum Bake-out

After determining the initial vacuum treatment was inadequate to prepare the samples for experimentation, most of the vessels were disassembled and loaded individually or in pairs into the vacuum tube furnace (described in Section 2.7) and heated to an internal temperature of 350°C which required a surface temperature of 450°C. The off gas from the parts was monitored using an attached residual gas analyzer. Figures 17 and 18 show the vacuum and pressure characteristics for the Cr plated CFVA components. Note the pressure was not permitted to exceed  $1.5 \times 10^{-6}$  Torr during heating and the pressure at the end of the heat treatment was  $1 \times 10^{-7}$  Torr compared to the starting pressure of  $7 \times 10^{-8}$  Torr. Table 3 summarizes the bake out results for starting pressure, time, and ending pressure. The starting and ending pressure were intended to be within a factor of two of each other; however this target was not always achieved. The integral of the time-pressure data was obtained to estimate the hydrogen load in the samples. As can be seen, there is a significant hydrogen content that scales with the duration of the extraction, as expected.

As can be seen from the data, the coated CFVA components required multiple days of heating to remain below  $1.5 \times 10^{-6}$  Torr and multiple days to achieve the target pressure. Despite these treatments, the performance of the Restek bottles was superior to all the experimental coatings and treatments evaluated in this study, with the exception of the Al 6061 aluminum CFVA.



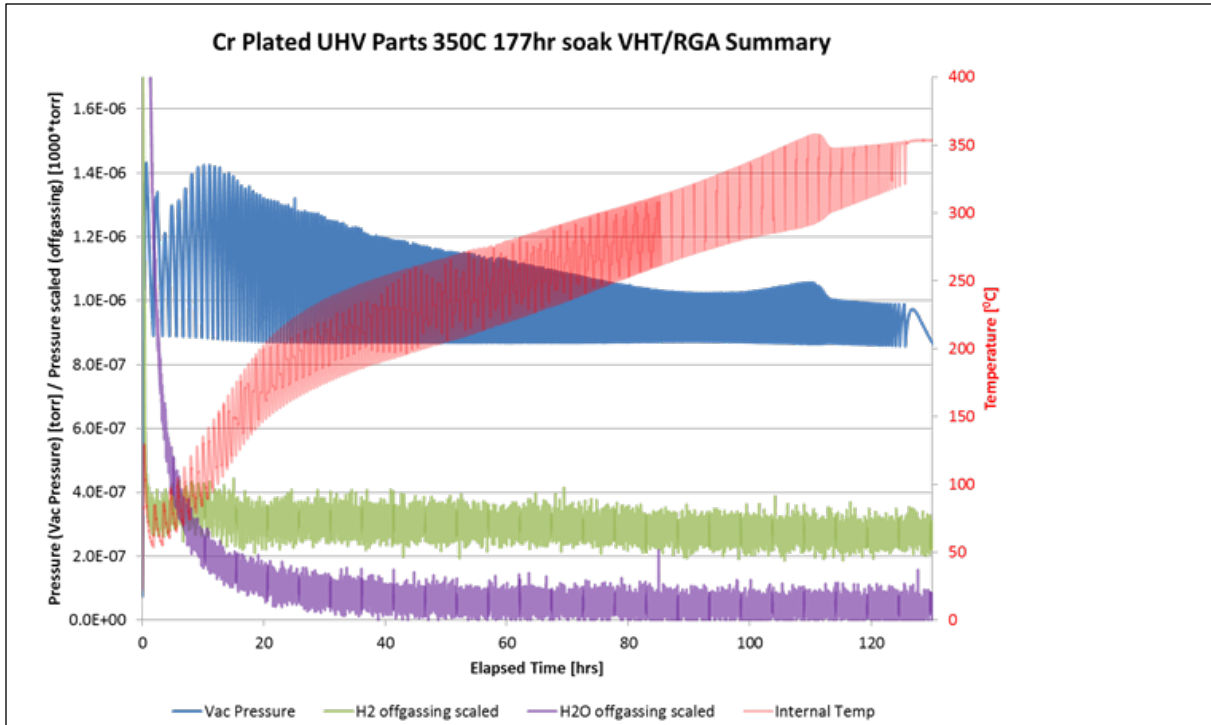


Figure 17

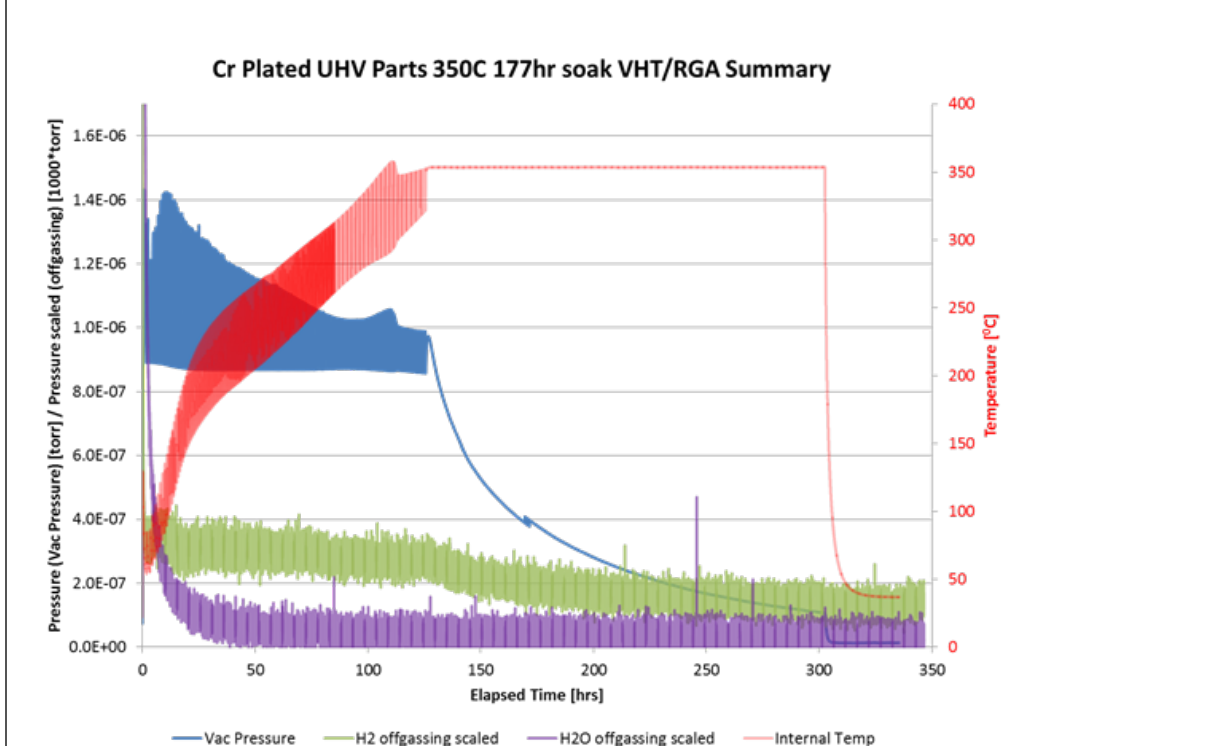


Figure 18

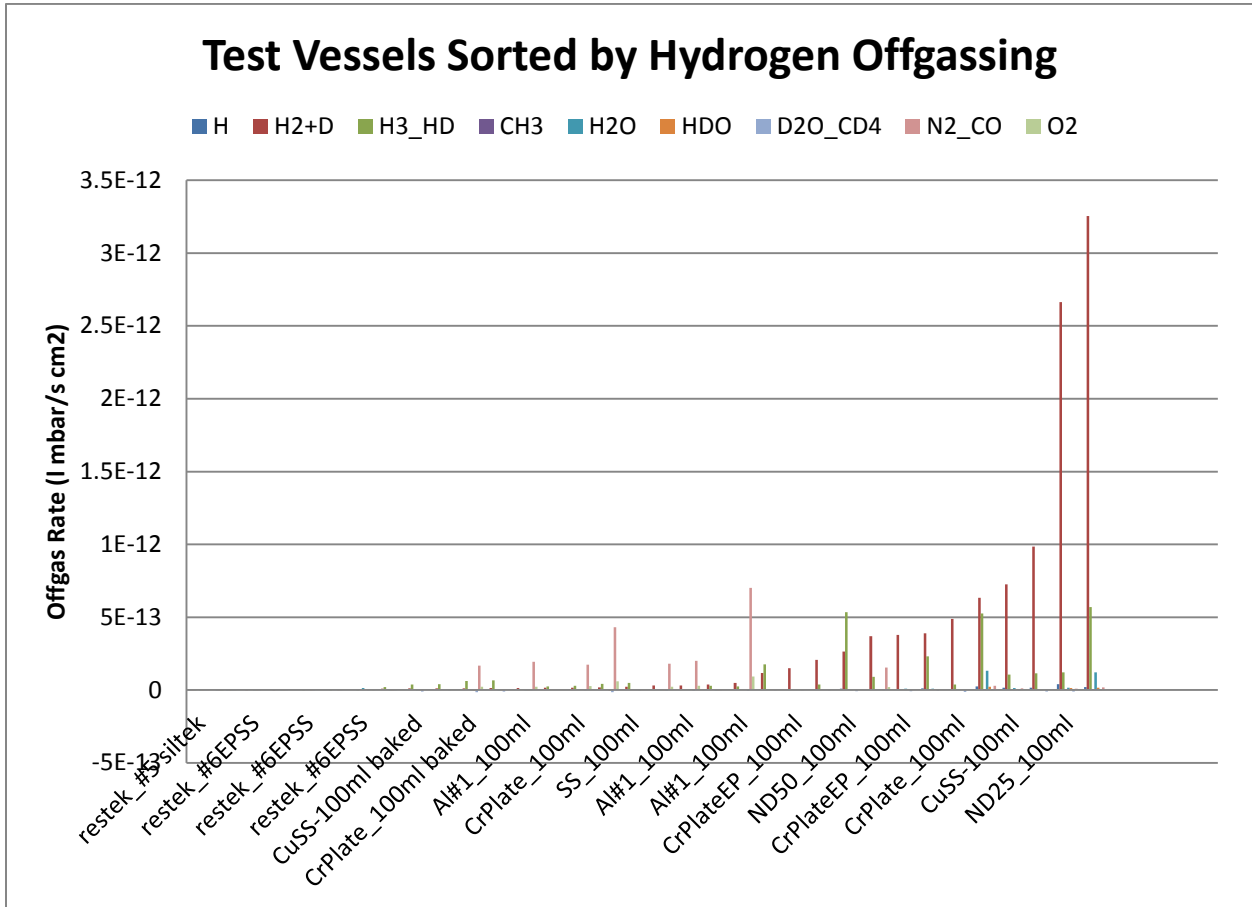
**Table 3 Tube Furnace Bake out Summary**

ID	Init P (Torr)	Max P (Torr)	Ramp (days)	Soak time (days)	Total Time (days)	Final P (Torr)	Pressure integral Tor
CFVA SS	1.39E-08	2.05E-06	0.06	3.65	3.71	3.41E-07	4.42E-06
CFVA Cr Plate	7.47E-08	1.41E-06	5.18	7.43	12.61	1.07E-07	1.85E-04
CFVA Cu 25ND	1.81E-08	1.71E-06	3.11	5.17	8.28	1.20E-07	1.17E-04
CFVA Cu 50ND	3.10E-08	1.43E-06	6.12	11.58	17.69	6.35E-08	2.12E-04

### 3.5 Data Summaries

Figures 19-22 chart the data results in terms of H<sub>2</sub>, HD, Air, and Water leak rates.

Table 4 summarizes the leak rate determined for selected ions.



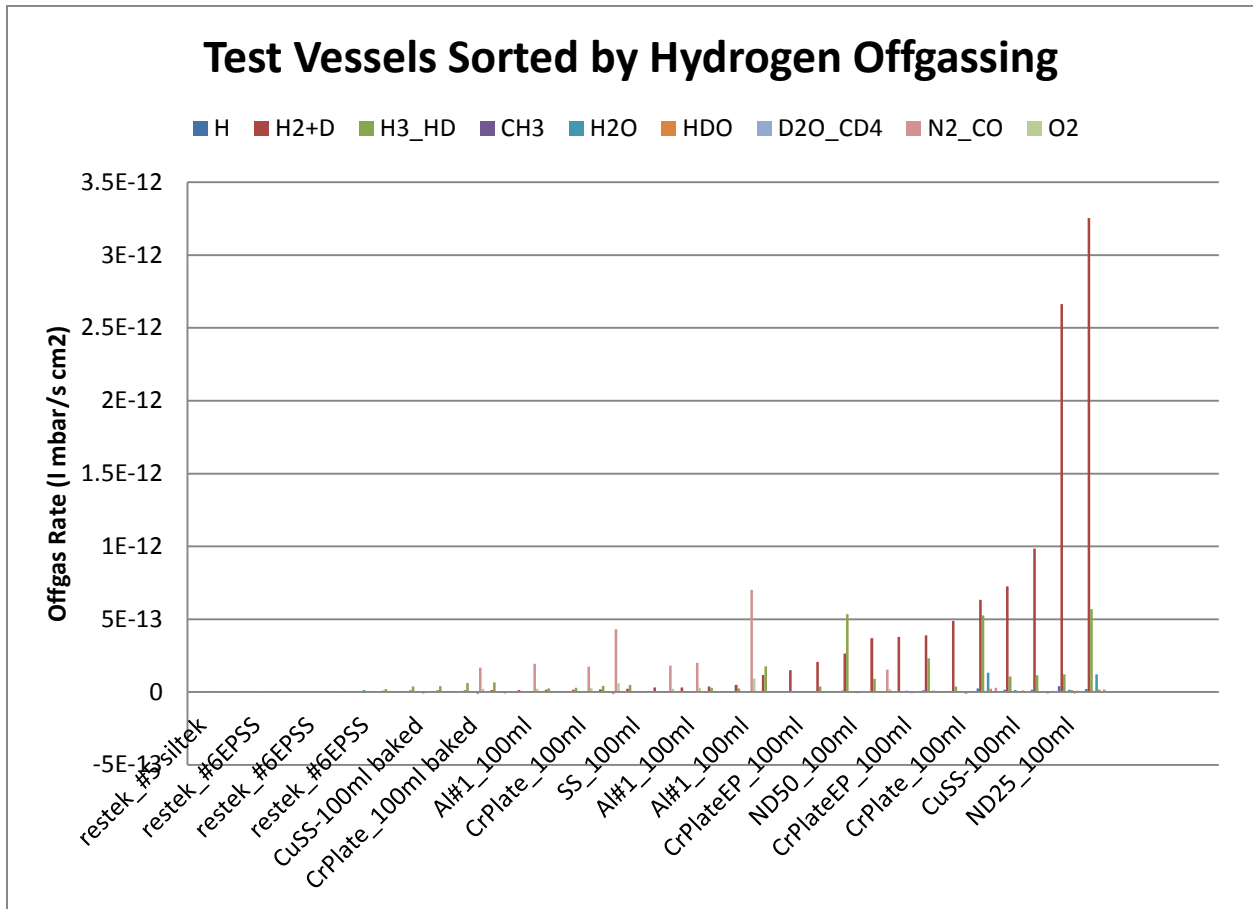
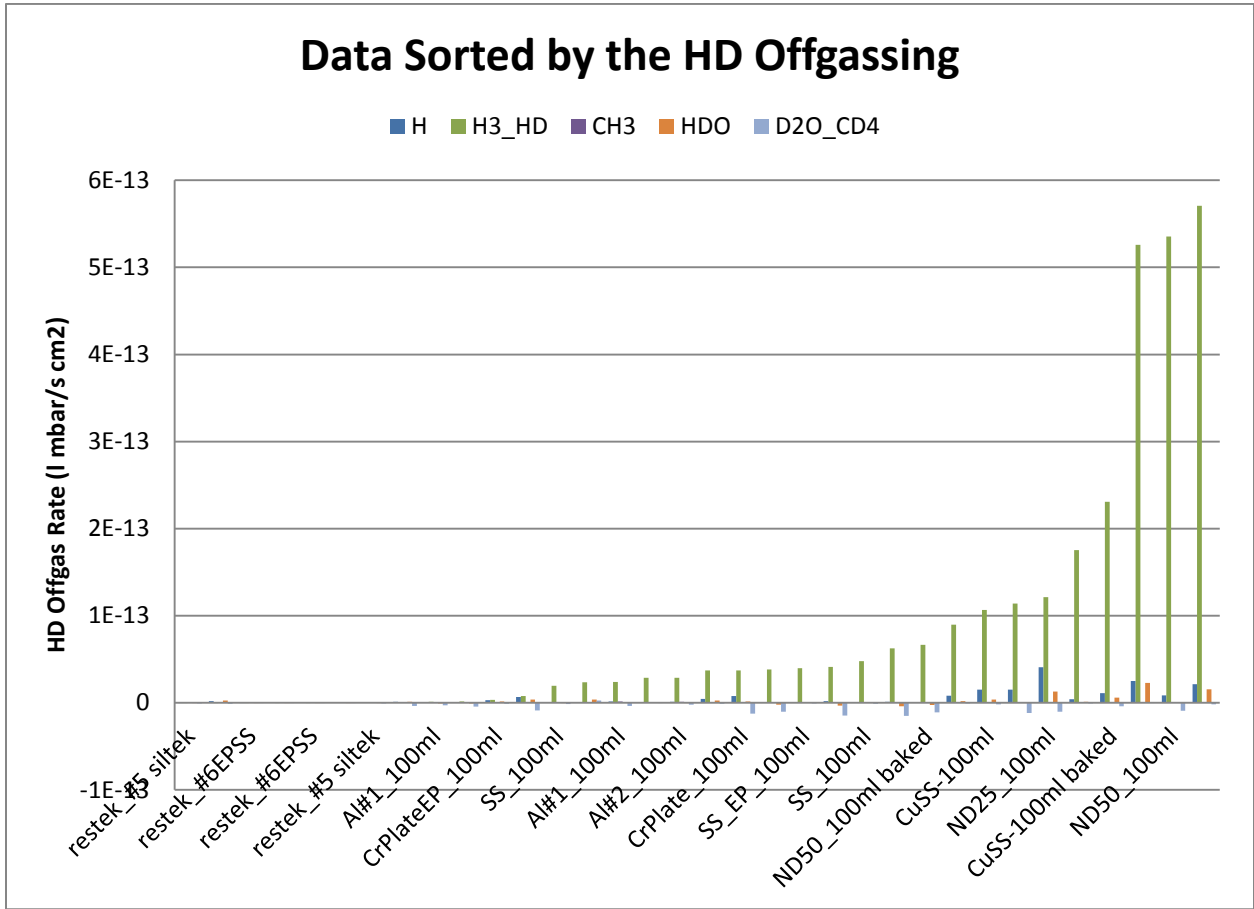


Figure 20 Hydrogen Off gas Rate



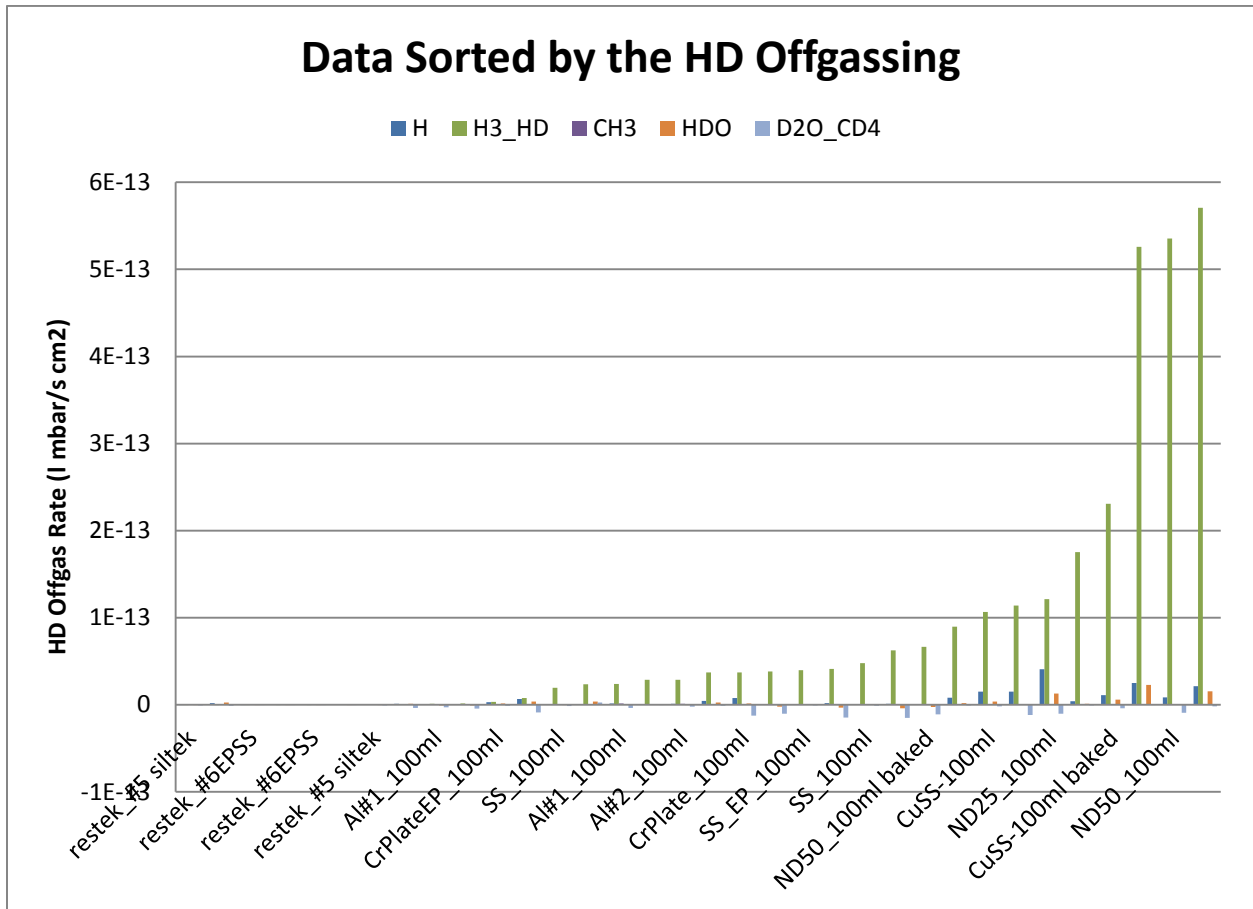
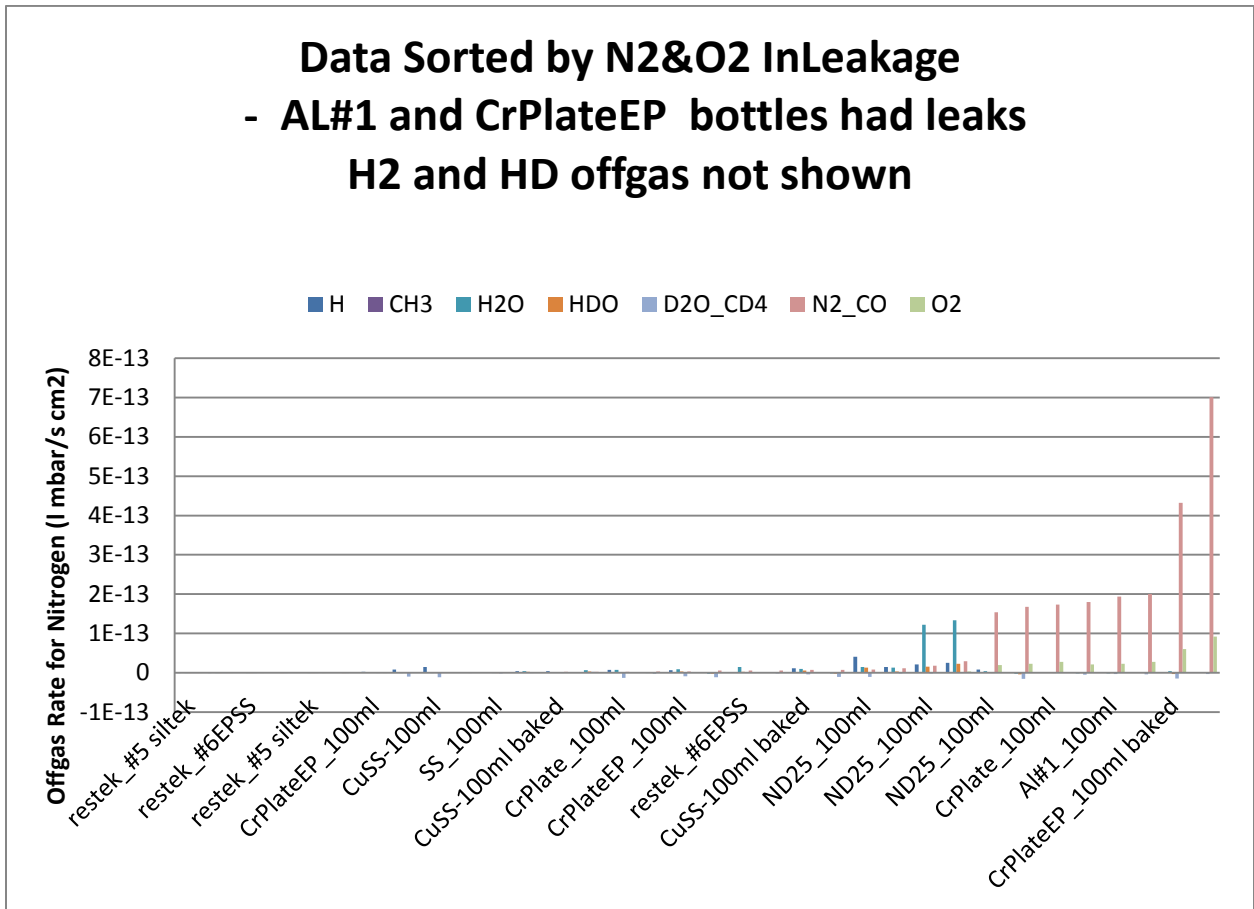


Figure 21 HD Off gas Rate



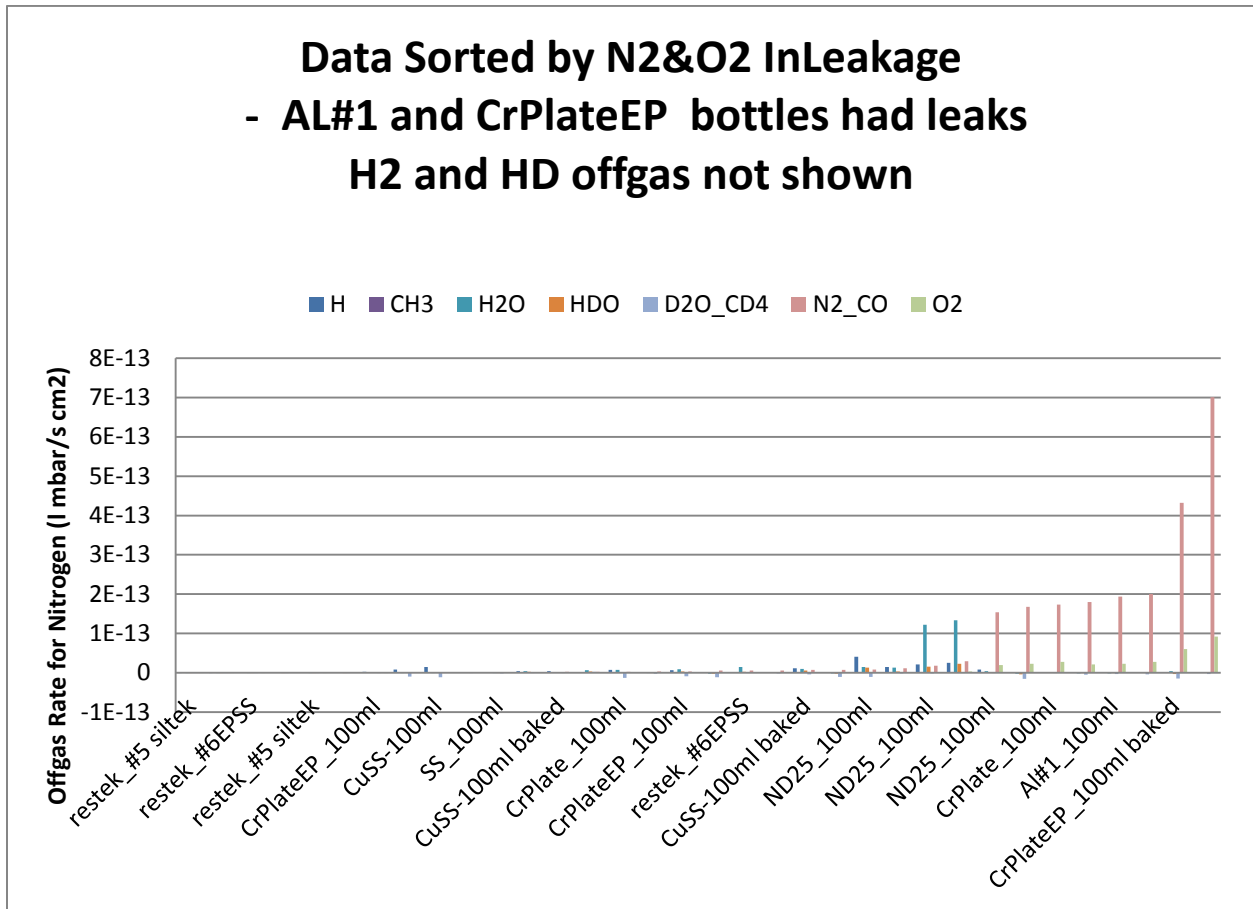
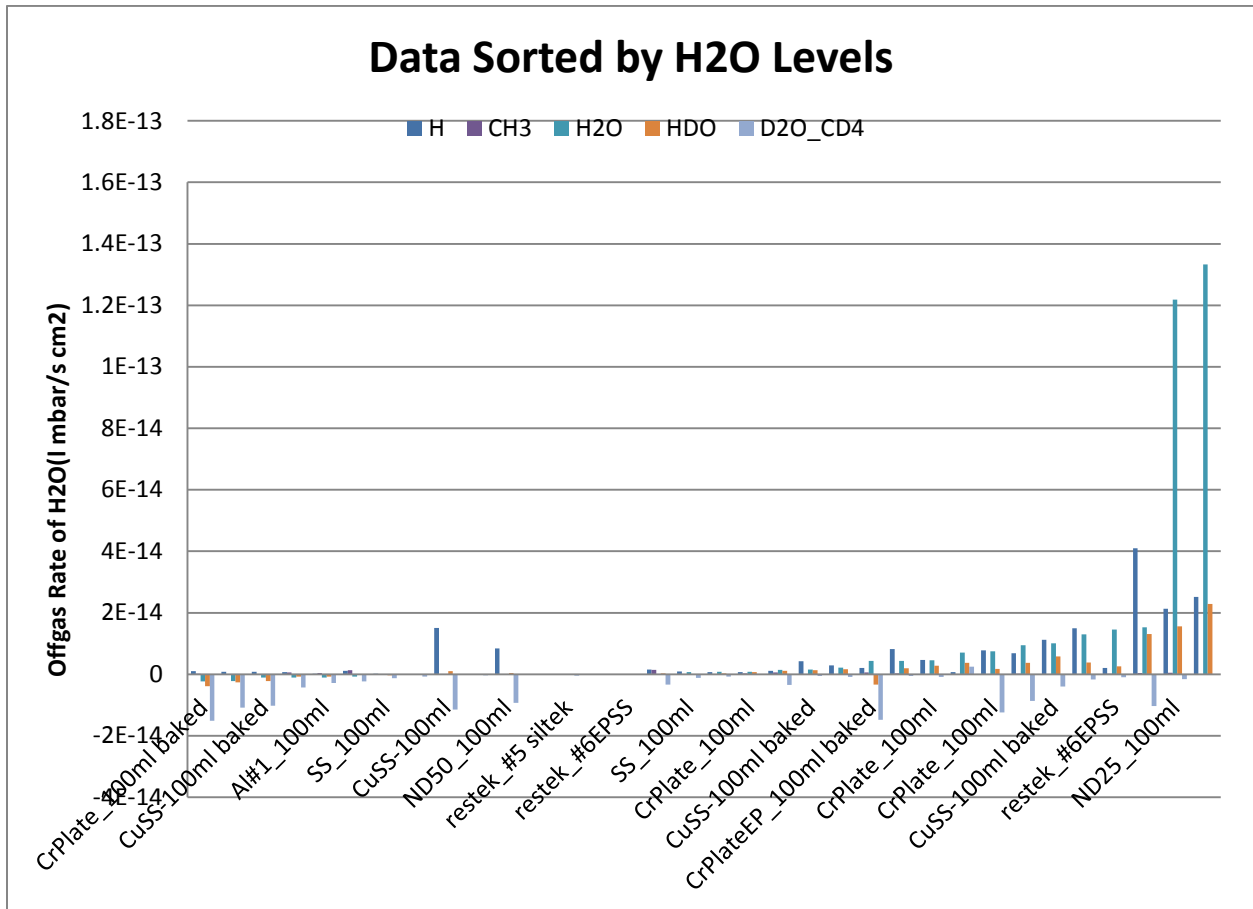


Figure 22 Some of the test containers had air leakage. To see the effect the larger H2 and HD data is not shown in this data set.





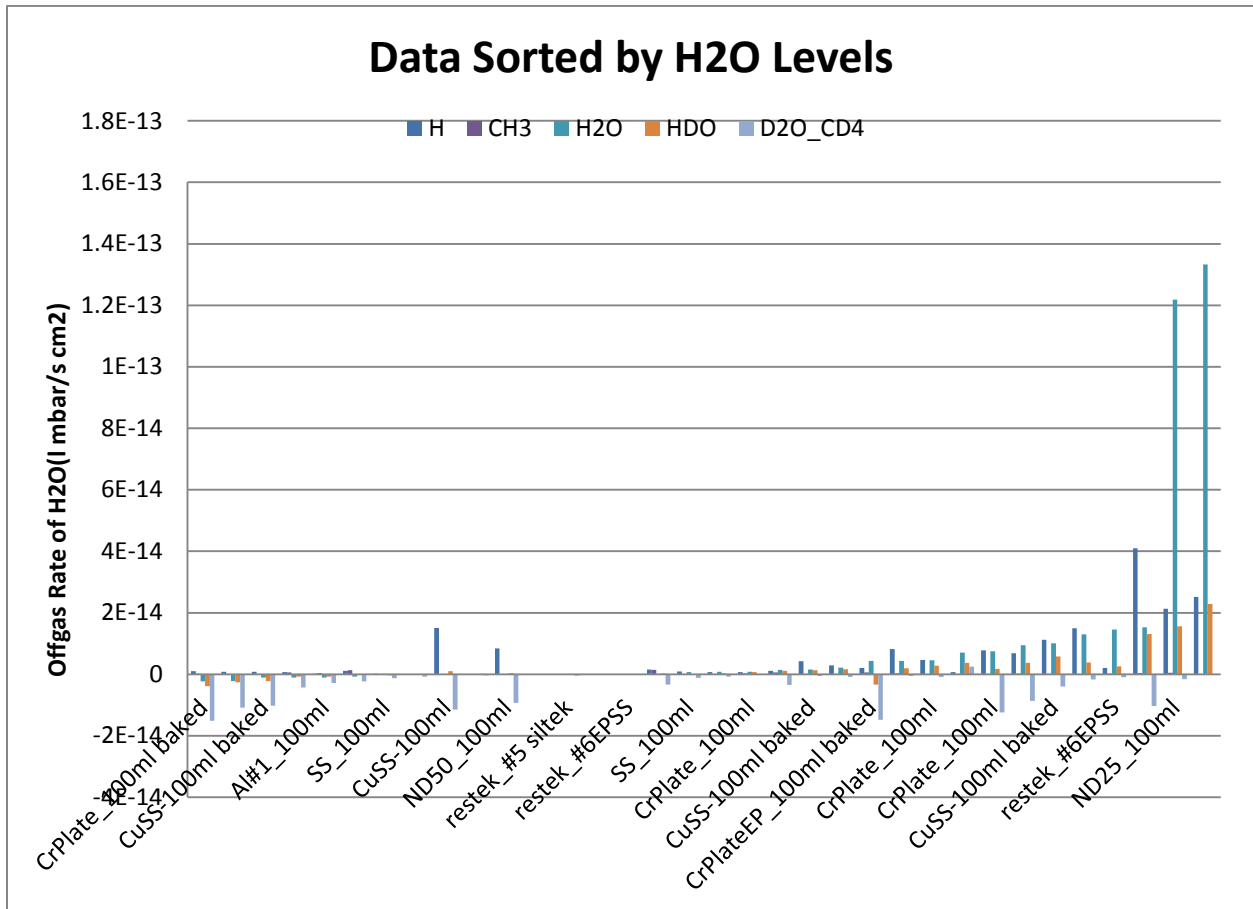
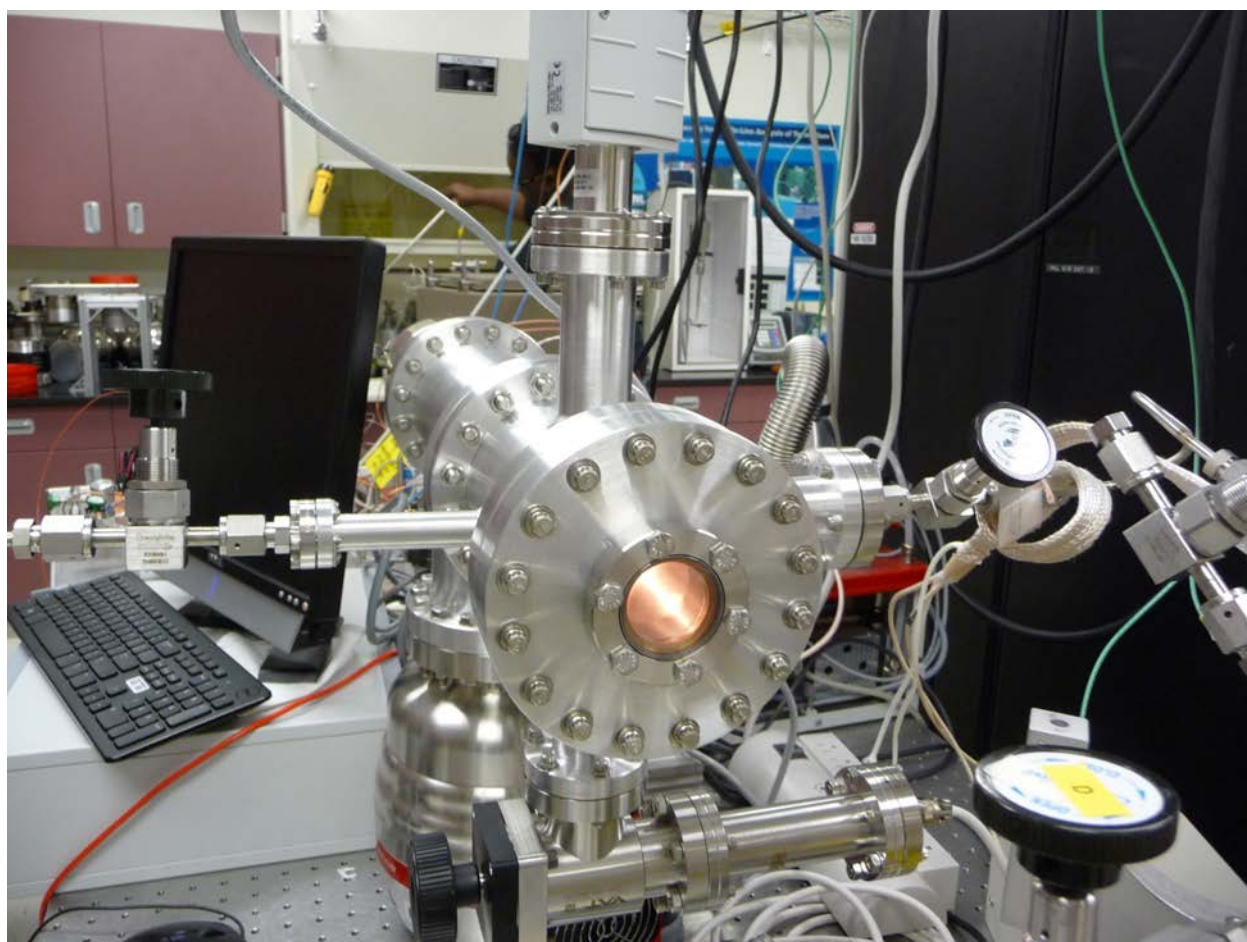


Figure 23 Baking out clearly reduced residual water in the samples and some coatings held water.

### 3.6 Aluminum Housings and Vessels

During these studies several observations were made about using aluminum vacuum parts. The mass spectrometer was housed in an Al 6061 all-aluminum set of vacuum flanges obtained from Accurate Machining and Tools, Oak Ridge, TN as shown in Figure 24. The housing initially achieved extremely low vacuum levels that were below that measurable with our Pfeiffer hot cathode gauge and were below  $5 \times 10^{-10}$  mbar. Over time the housing performed not as well and each time the system had to be opened to replace a filament or otherwise exposed to the laboratory atmosphere which made subsequent pump downs take longer. It is suspected that the aluminum surface has begun to age and to create an activated alumina surface layer. This layer acts as a getter collecting all of the trace vapors in the laboratory atmosphere.

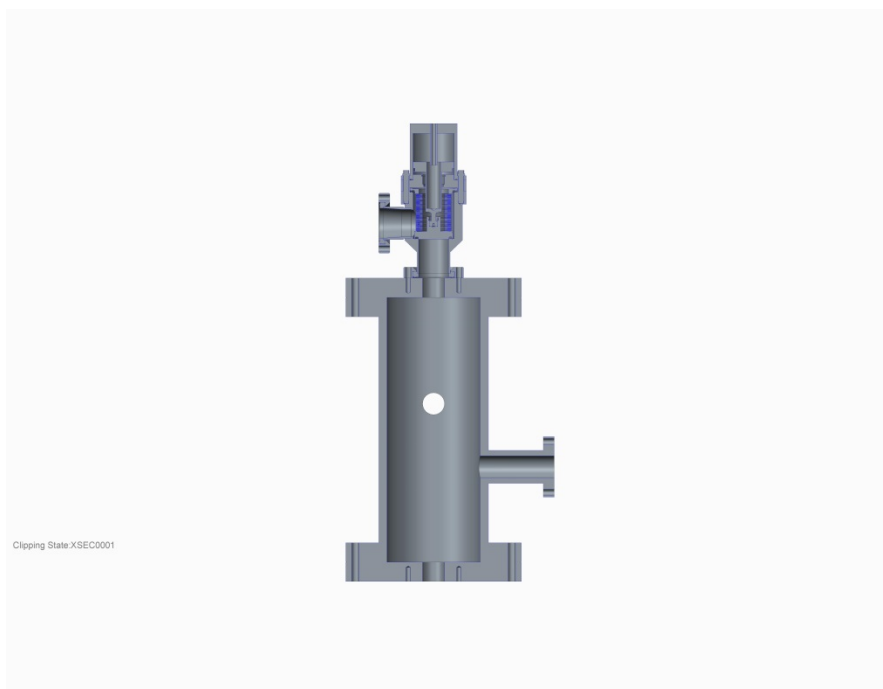


**Figure 24 Aluminum housing was used for the mass spectrometer.**

Aluminum CF flanges tend to have a problem with thermal expansion. Connection fittings frequently had to be re-tightened to improve the seals after low temperature thermal desorption treatments. This need was a potential problem since the aluminum knife edges are much softer than those of stainless steel CF. Aluminum gaskets were preferred to the standard copper ones, but can only be used once. In addition, the knife edges were easily damaged. As a result of these shortcomings, it was not uncommon to have leaks develop in the aluminum CFVA and vacuum housings. Once the leaks were sealed, i.e., the bolts were tightened, the Al vacuum components generally performed well.

Another potential issue with aluminum components is that the maximum operating temperatures are less than half that of stainless steel components. Aluminum will soften and melt around 660°C long before stainless steel at 1350°C. This difference in temperature capability is a potential problem if aluminum is specified for containment of tritium used for air flights and subsequent accident release calculations. A secondary sleeve of steel might be required to assure vessel qualification. On the other hand companies such as Luxfer, Inc. have used aluminum vessels at high pressures for scuba, beverage, and other applications and high pressure mixed gas standards with hydrogen, deuterium, and C1-C4 hydrocarbons have been stable in Luxfer's bottles for over two years in our laboratory, although an additional challenge with commercial Al alloy gas standard bottles is valve attachment. Most Al bottles use threaded valve bodies to attach to the bottle with an elastomer seal. Elastomer seals are not a preferred sealing material for tritium or hydrogen.

As part of this project an aluminum 3 liter expansion volume was designed as shown in Figure 25. However experience with the existing housing and the need to fully qualify the welding, pressure, and design specifications led to a decision to withhold pursuing procurement of the component.



**Figure 25 Cross Sectional view for a potential all aluminum 3 liter expansion volume.**

## 4.0 Conclusions

These tests indicate that depletion of hydrogen from vessel walls is critical to achieving low off gassing rates. Coating techniques even when performed at high temperatures frequently led to hydrogen generation and trapping into the vessel walls. Hydrogen uptake was observed in high temperature aluminide and chromide coating applications. Hydrogen uptake was also observed in chromium electroplating and electroless copper/nano-diamond coatings. Hydrogen levels were well above those found in the starting base stainless steel. Extracting the hydrogen from these materials required extended thermal treatment at high vacuum conditions. Once vacuum treated to be free of internal hydrogen and surface adsorbed moisture, the CFVA with the chromium coating and the Al 6061 aluminum CFVA exhibited promising results in minimizing water formation as well as having fewer exchange sites to form HD. These materials performed similarly to clean and hydrogen depleted stainless steel vessels.

The electro-polished and ultra-clean stainless steel gas sample bottles such as those obtained from Restek and previously tested CTCVs from Tek-Vac performed as well as, or better than the alternative coatings. Based on this research, to prepare an acceptable alternative coated vessel, the vessel requires similar cleaning and hydrogen removal treatments as the base stainless steel components. It is critical that the

components be treated to remove the internal hydrogen. As a result our studies indicate little advantage to using these alternative coatings due to the significant effort required for qualification and uncertain benefits.

Finally, the experience with aluminum vacuum housings has shown both good and bad results. Aluminum vacuum housings tend to pump down quickly and achieve excellent vacuum characteristics after an initial light vacuum bake out, when initially placed in service. However, extended and repeated bake outs, 100-150°C, tend to create an active adsorbent surface that upon exposure to atmosphere rapidly adsorbs trace vapors which have to be subsequently baked out. Our experience has been that the surface becomes more active over time as the aluminum surface ages.

## **5.0 Recommendations, Path Forward or Future Work**

These studies indicate that Type 304L SS which has been properly thermally treated and cleaned will work as well or better than most alternative coatings studied and at lower cost and with simpler treatments. The focus of continued research should be to develop standard non-proprietary treatment processes for cleaning, electro-polishing, degassing, and possible oxidative treatment for chromium surface enhancement. A second PDRD project to study direct treatment of stainless steel is in progress.

Aluminum based components showed promise and new vendors and material sources may enter the supply market. Vessels that minimize fittings should be pursued. Welded aluminum may be a good option for seals as new clean welding techniques are developed for aluminum applications. Future opportunities to use aluminum might become viable.

Several possible coatings were not fully investigated. A few coupons were sputter coated with gold and thermally extracted. These coupons released the same amount of hydrogen as an untreated sample but there is literature data (Gill) that reports some success with gold coatings. Our laboratory has experts in gold nano-particulates and coupons were also coated with Au NPs. These samples also released the comparable levels of hydrogen as the bare coupons. In addition, the Au-NP was not continuous which makes for poor permeation resistance. Thus, further development would be necessary to improve the surface coverage. In addition, any method that relies on oxidation and reduction reactions may promote the formation of hydrogen which can cause similar problems to those observed with this work.

These studies indicate that surface exchange of H and D can be important. Fundamental studies of the exchange source should be conducted checking exchanges with bound water, hydroxide, hydrocarbons, and amines or nitride bound hydrogen. A focus should be on tritium exchanges which generally occur faster than deuterium. The heavier tritium atom results in shorter bond distances. Tritium provides electrons and activated free radicals to accelerate exchanges.

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## 7.0 Appendix

Table 4 Off gas Rates for Selected Ion Mass (m) – Units of mbar\_l/s\_cm<sup>2</sup>

Bottle	Time (days)	Time (sec)	H (m=1)	H2+D (m=2)	H3_HD (m=3)	CH3 (m=15)	H2O (m=18)	HDO (m=19)	D2O_CD4 (m=20)	N2_CO (m=29)	O2 (m=32)
Al#1_100ml	6.090	526217.9	1.57E-15	4.89E-14	2.42E-14	1.47E-15	1.01E-16	3.23E-16	-3.4E-15	7.01E-13	9.18E-14
Al#1_100ml	10.099	872512.1	6.64E-16	3.07E-14	1.56E-15	6.3E-16	-1.1E-15	-7.1E-16	-4.3E-15	1.8E-13	2.16E-14
Al#1_100ml	13.900	1200950	1.09E-15	3.14E-14	8.15E-16	6.4E-16	1.43E-15	1.12E-15	-3.5E-15	2E-13	2.81E-14
Al#1_100ml	14.064	1215172	2.36E-16	1.42E-14	1.04E-15	3.78E-16	-1E-15	-7.5E-16	-2.8E-15	1.94E-13	2.31E-14
Al#2_100ml	14.091	1217498	1.13E-15	3.76E-14	2.89E-14	1.37E-15	-7.9E-16	-2E-16	-2.3E-15	3.66E-15	6.54E-17
CrPlate_100ml	4.955	428122.7	7.83E-15	4.87E-13	3.73E-14	9.33E-17	7.51E-15	1.75E-15	-1.2E-14	2.9E-15	4.02E-16
CrPlate_100ml	47.663	4118091	4.66E-15	2.06E-13	3.73E-14	2E-17	4.59E-15	2.81E-15	-8.5E-16	2.21E-15	1.33E-16
CrPlate_100ml	99.891	8630581	7.51E-16	1.62E-14	2.87E-14	3.07E-16	8.47E-16	6.63E-16	-1.3E-16	1.73E-13	2.76E-14
CrPlate_100ml baked	6.925	598314.7	1.03E-15	1.17E-14	6.26E-14	2.23E-16	-2.3E-15	-3.9E-15	-1.5E-14	1.68E-13	2.3E-14
CrPlateEP_100ml	4.984	430609	6.81E-15	3.79E-13	7.66E-15	1.69E-16	9.42E-15	3.72E-15	-8.7E-15	3.85E-15	2.53E-16
CrPlateEP_100ml	47.675	4119128	2.89E-15	1.49E-13	3.27E-15	1.13E-17	2.19E-15	1.66E-15	-8.4E-16	4.5E-16	-7.4E-19
CrPlateEP_100ml baked	6.908	596830.9	2.1E-15	1.7E-14	4.12E-14	6.06E-16	4.35E-15	-3.3E-15	-1.5E-14	4.32E-13	6.02E-14
CuSS-100ml	6.812	588535	1.51E-14	9.86E-13	1.14E-13	4.77E-17	-1E-16	9.8E-16	-1.2E-14	1.45E-15	9.3E-18
CuSS-100ml	42.799	3697805	1.5E-14	7.26E-13	1.07E-13	6.19E-17	1.29E-14	3.79E-15	-1.7E-15	1.14E-14	1.21E-15
CuSS-100ml baked	6.893	595588.4	8.34E-16	1.06E-14	3.84E-14	4.82E-17	-1.1E-15	-2.2E-15	-1E-14	7.36E-15	2.84E-17
CuSS-100ml baked	15.801	1365223	1.12E-14	3.9E-13	2.31E-13	3.45E-17	1.01E-14	5.85E-15	-4E-15	7.22E-15	2.85E-16
CuSS-100ml baked	69.941	6042871	4.22E-15	1.16E-13	1.75E-13	1.41E-17	1.53E-15	1.34E-15	-5.5E-16	2.44E-15	4.82E-18
ND25_100ml	6.812	588535	4.1E-14	2.66E-12	1.21E-13	4.18E-16	1.52E-14	1.31E-14	-1E-14	8.26E-15	2.38E-17
ND25_100ml	42.799	3697805	2.13E-14	3.26E-12	5.71E-13	4.74E-16	1.22E-13	1.56E-14	-1.6E-15	1.85E-14	1.15E-15
ND25_100ml	104.818	9056253	8.16E-15	3.69E-13	8.99E-14	2.49E-16	4.37E-15	2E-15	-5.5E-16	1.54E-13	1.95E-14
ND50_100ml	6.956	600970.1	8.41E-15	2.64E-13	5.35E-13	8.3E-17	-6.1E-17	4.19E-16	-9.2E-15	1.43E-15	4.68E-17
ND50_100ml	35.937	3104981	2.51E-14	6.33E-13	5.26E-13	9.84E-17	1.33E-13	2.29E-14	-1.6E-16	2.98E-14	3.18E-15

ND50_100ml baked	6.932	598955.2	8.25E-16	1.36E-14	6.67E-14	3.37E-17	-2.2E-15	-2.6E-15	-1.1E-14	5.66E-15	4.48E-18
SS_100ml	11.976	1034732	2.02E-16	8.44E-15	1.96E-14	8.55E-18	-1.2E-16	-3.5E-16	-1.3E-15	2.14E-15	1.28E-16
SS_100ml	53.990	4664777	9.47E-16	2.2E-14	4.79E-14	9.37E-18	7.54E-16	1.04E-16	-1.2E-15	6.27E-15	5.24E-16
SS_EP_100ml	11.956	1032981	7.29E-16	1.58E-14	2.36E-14	6.07E-17	7.04E-15	3.72E-15	2.51E-15	2.55E-15	2.24E-16
SS_EP_100ml	53.979	4663792	7.13E-16	1.09E-14	3.97E-14	5.82E-18	8.21E-16	2.59E-16	-7E-16	1.6E-15	1.7E-16
restek_#5 siltek	11.913	1029253	-4E-17	-7.7E-16	-2.6E-16	2.55E-18	-9.3E-18	-1.5E-16	-4.7E-16	-1.6E-16	-5.5E-19
restek_#5 siltek	53.141	4591425	9.05E-18	-4.5E-17	1.13E-16	1.46E-18	-1.1E-16	-2.1E-16	-7.8E-16	7.91E-17	-1.2E-18
restek_#5 siltek	111.100	9599036	7.67E-18	6.62E-17	-1.8E-17	4.42E-19	4.4E-19	-5E-18	-1.6E-16	7.99E-17	2.76E-18
restek_#6EPSS	11.943	1031848	2.04E-15	3.58E-16	-1.7E-16	1.61E-16	1.46E-14	2.6E-15	-9.7E-16	5.97E-15	-2E-18
restek_#6EPSS	53.188	4595420	-1.9E-17	-1.8E-16	-5.4E-17	4.99E-19	-4.3E-17	-6.6E-17	-1.2E-16	-3.9E-17	-1.2E-18
restek_#6EPSS	111.100	9599036	1.79E-18	-6.1E-17	3.64E-17	4.97E-19	-7E-17	-9.9E-17	-3.7E-16	2.24E-17	-7.6E-19
restek_#6EPSS	147.196	1271773	6.29E-18	1.18E-17	-9.3E-18	4.79E-19	6.91E-18	-7.4E-18	-1.6E-16	7.63E-17	2.4E-18

**8.0 Distribution:**

R.P. Addis, 7773-A  
M.J. Barnes, 773-A  
D.W. Babineau, 999-2W  
J.E. Halverson, 999-2W  
B.A. Ferguson, 235-H  
R.W. Allgood Jr., 246-1H  
T.J. Worrell, 246-1H  
D.B. Carroll, 246-1H  
J. D. Westergreen, 235-H  
C.B. Mauldin, 246-2H  
M.L. Whitehead, 246-2H  
C.M. Gregory, 773-A  
J.M. Newell, 246-H  
R.B. Wyrwas, 999-2W  
Dien Li, 773-42A  
E.A. Stein, 999-W  
D.A. Hitchcock, 999-2W  
B. Peters, 999-2W

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