

# **Water-Stimulated Tritium Release from Metals**

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## **Abstract**

Experiments have been carried out to understand how tritium, a radioactive isotope of hydrogen, desorbs from, or leaves, metal surfaces. In the experiment, a tritium-contaminated metal coupon is exposed to a gas stream and the radioactivity removed from the coupon is carried by the gas stream and bubbled into a liquid scintillation cocktail for counting. From this measurement, the rate of tritium outgassing is calculated and plotted as a function of time. The outgassing rate was measured as a function of the humidity of the gas stream, the temperature of the oven in which the coupon is held, and the chemical composition of the metal coupon used. A goal of the experiments was to measure the steady desorption rates at a given temperature and humidity. Specifically, the present experimental purpose was to measure how tritium desorption is affected at modest temperatures ( $40^{\circ}\text{C} \rightarrow 130^{\circ}\text{C}$ ) and relative humidity (0-40%RH). These experiments demonstrated that the rate of tritium desorption increases with increasing temperature and humidity. It was also concluded that the tritium removed at these temperatures emanated from only the near-surface layers of the metal. The results of these experiments were found to be reproducible.

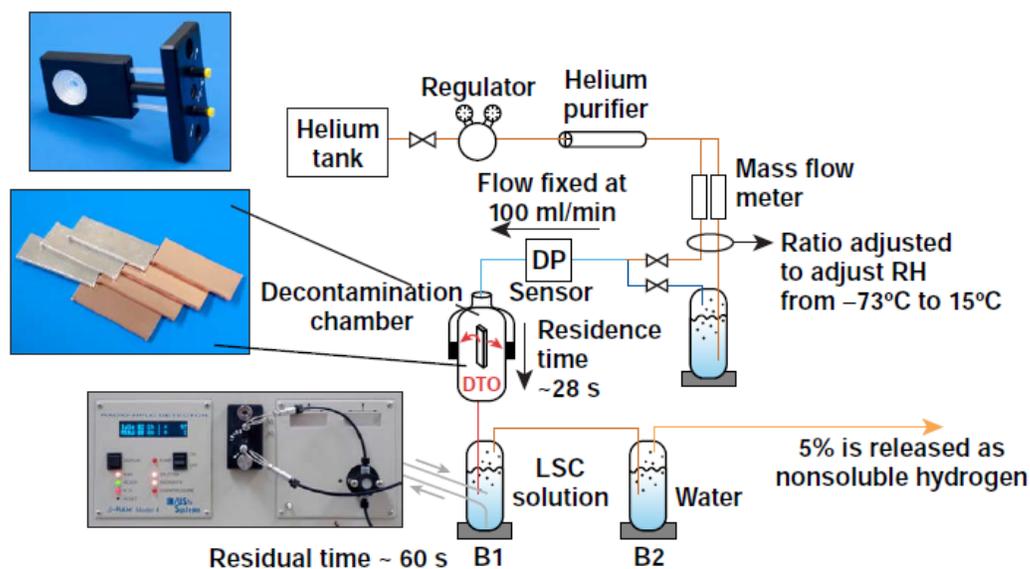
## **Introduction**

Tritium is a radioactive isotope of hydrogen that has applications in nuclear fusion. Tritium contaminates metal surfaces found in the area in which it is being used. Through a process called adsorption, tritium forms a chemical bond with a surface in a process known as chemisorption or is held to the surface by weaker inter-molecular attractive forces in a process known as physisorption. The accumulation of adsorbed tritium creates one or more monolayers on a surface. The first monolayer of tritium is often chemisorbed, while subsequent layers are physisorbed.

Tritium contamination poses a health hazard to radiation workers. Tritium can adsorb onto and desorb from surfaces as a pure gas ( $T_2$ ); however, it is more commonly found in the place of a protium molecule in water, such as in HTO. More generally, the adsorption and desorption of water have numerous other applications. For one, water desorption off metals can act as a contaminant in ultra-pure gas streams used in industrial settings. Water can desorb off the inner surfaces of process lines into streams used in the fabrication of semi-conductor chips. The water can then adsorb onto the surface of these chips and reduce their lifespan and reliability<sup>(1,2,3)</sup>. Another application of note is water adsorption onto metal surfaces as a cause of corrosion. Building metal can be corroded through the adsorption of water layers onto the metal surface. These water layers can then absorb contaminants such as hydrogen sulfide ( $H_2S$ ), causing the formation of acidic water, which can corrode the metal. Research has been performed examining ways to prevent water adsorption onto metal surfaces, such as the use of copper (I) sulfide to prevent adsorption onto a copper surface. The adsorption of water layers on the cryogenic targets used in the Omega Laser System can reduce the neutron yield of inertial confinement fusion implosions. Previous reports<sup>(4,5)</sup> have examined the dependence of tritium outgassing rates on humidity at higher temperatures.

The present experiments studied tritium desorption off copper and stainless steel coupons at temperatures below  $130^\circ C$  and RH below 40% by heating and exposing the samples to water vapor simultaneously. The dependence of desorption rates on low temperatures for a range of humidities was measured.

## Experimental Setup



*Fig 1: A representation of the experimental setup. The decontamination chamber also serves as an oven.*

A schematic of the experiment is shown in Fig. 1. The experiment begins with a tank of compressed helium gas. Gas passes from a line beginning at the tank to a regulator, through which the pressure of the gas stream is reduced to about 20 psi. The gas stream then passes through a helium purifier, which removes any initial humidity or other contaminants that may exist in the stream. The stream is then split and passed to two mass flow meters. One of the mass flow meters passes helium to a humidifier allowing water to enter the stream; the other meter does not pass the stream to a humidifier, ensuring that this portion of the gas stream remains dry. The meters allow the amount of gas passed through each respective stream to be controlled. The total flow rate used in the experiment is always 100 mL/min; however, this total flow can be split in different ratios between the humidified and dry streams.

Following splitting and passing through the mass flow meters, the streams are rejoined and run through a digital dew point (DP) sensor, allowing the humidity to be monitored. The gas stream is then passed under a fume hood and into an oven where the temperature of the stream can be varied. Thermocouples are used to measure the temperature inside the oven. Also inside the oven is a metal coupon that has been exposed to tritium. Exposure of the gas stream to the coupon inside the oven allows tritium to desorb off the coupon and into the gas stream. Plastic tubing then runs the gas stream through two consecutive bubblers each containing liquid scintillation cocktail. The efficiency of each bubbler in collecting tritium is 90% and, thus, their combined efficiency is 99%. Therefore, the gas can then be safely emitted into the fume hood.

The cocktail is continuously sampled using the  $\beta$ -Ram system. When tritium decays to emit a  $\beta$  particle, the cocktail emits a photon, causing a flash of light which can be counted to provide a measure of the activity of the cocktail sampled and, therefore, the tritium that desorbed from the metal into the gas stream. Through the Scint Flow program, the number of fluoresces is recorded in a Microsoft Excel spreadsheet. The Oven Control program written in LabView controls the flow rate of the gas stream and the temperature of the oven. Tritium desorption rates are understood to be affected by three factors: the rate of diffusion from the bulk of the metal to the oxide layer, the rate of diffusion through the oxide layer and the rate of desorption from the surface oxide layer. Modeling of tritium desorption was performed by Jefferson Lee.<sup>(6)</sup>

### **Data Processing**

From the activity reading recorded in an Excel spreadsheet, a number of conversions are used including the counting efficiency of the  $\beta$ -Ram system, which is measured through the use of a calibrated liquid scintillation counter (LSC). The LSC gives the activity of the cocktail in

both CPM and decays per minute (DPM) by counting the number of fluoresces made by the cocktail over a certain time interval. One-milliliter samples of cocktail were collected from each of the two bubblers for processing in the LSC. Once these conversions are completed, the activity is given in a more conventional unit: microcuries ( $\mu\text{Ci}$ ). The data are then differentiated with respect to time to give the outgassing rate of tritium from the metal coupon in  $\text{nCi}/\text{cm}^2/\text{s}$ .

Data were then entered into the Mathcad function Supsmooth, which removes much of the experimental noise from the data. Noise is found within all data collected. It is not merely a consequence of the limitations of measurement taking; in actuality, the decay of tritium is statistical, occurring at inherently inconsistent rates, causing a large amount of the noise in the data. Tritium decay can occur in bursts, followed by periods of fewer decays afterwards. This causes fluctuations in the data, even though the activity of the LSC should only increase because activity is added only and not removed. Consequently, Supsmooth provides an essential function to the data processing of the experiment because the fluctuations recorded in the activity measure are amplified when a derivative is applied to give the outgassing rate. It is noted, however, that Supsmooth can remove some of the sharp inclines and declines that represent real data. This, in turn, can skew the perceived timing of changes made in the experimental system. Additionally, Supsmooth on some occasions removes data peaks. Because of this, some runs are processed using a boxcar smoothing method. This method works by averaging the value of every point on the graph with respect to a specified number of surrounding points. The typical number of points used in the averaging process is 5, two on either side of the data point being averaged. An example of boxcar smoothing is shown in Fig. 2.

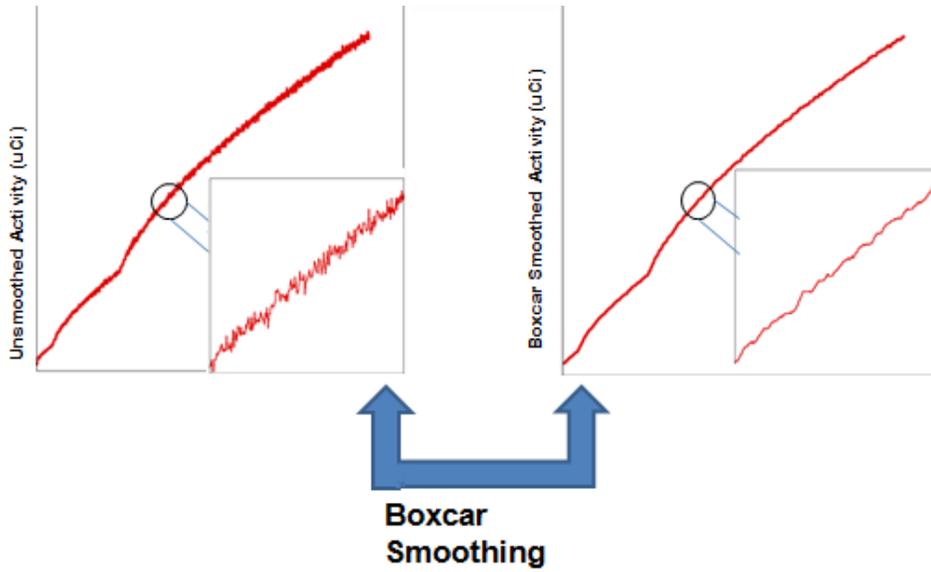


Fig 2: The effect of boxcar smoothing in removing data noise.

The noise of the resultant graphs is often greater for boxcar smoothed data compared to Supsmoothed data; however, this compromise is often necessary in order to preserve the information in the data.

In order to gain an accurate measure of the humidity in the system, the mass of the humidifying bubbler was recorded before and after experiments. The theoretical change in mass of the bubbler can be calculated using known experimental conditions through the use of the equation:

$$\frac{dm}{dt} = \frac{P_v F_{\text{carrier}}}{RT_s} * \frac{M_w}{\rho} \quad (1)$$

where  $P_v$  is the water vapor pressure,  $F_{\text{carrier}}$  is the flow rate of the humidified gas stream (liters/min),  $R$  is the universal gas constant,  $T_s$  is the temperature of the gas,  $M_w$  is the molar mass of water and  $\rho$  is the density of water (g/mL).

## Dependence of Outgassing Rate on Temperature

A run was conducted with the relative humidity being held constant, but with changes made to the temperature. The run was conducted using a relative humidity of 40% with temperatures ranging from 100°C-130°C and increasing in ten degree steps. This makes it possible to see the effect of increases in temperature with a fixed humidity. The supsmoothed outgassing rates of this run are shown in Fig. 3.

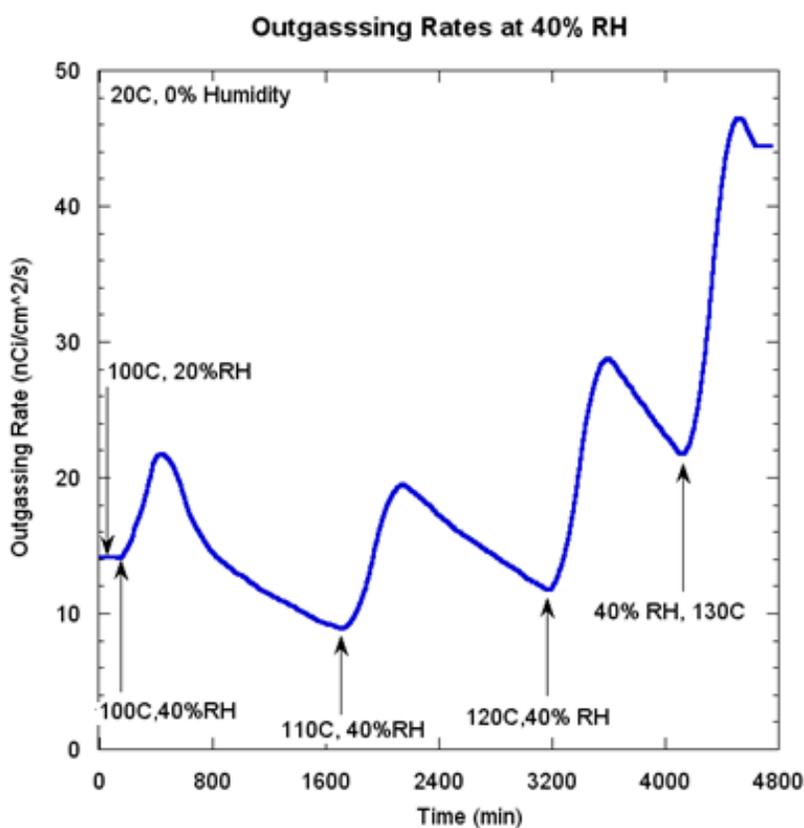
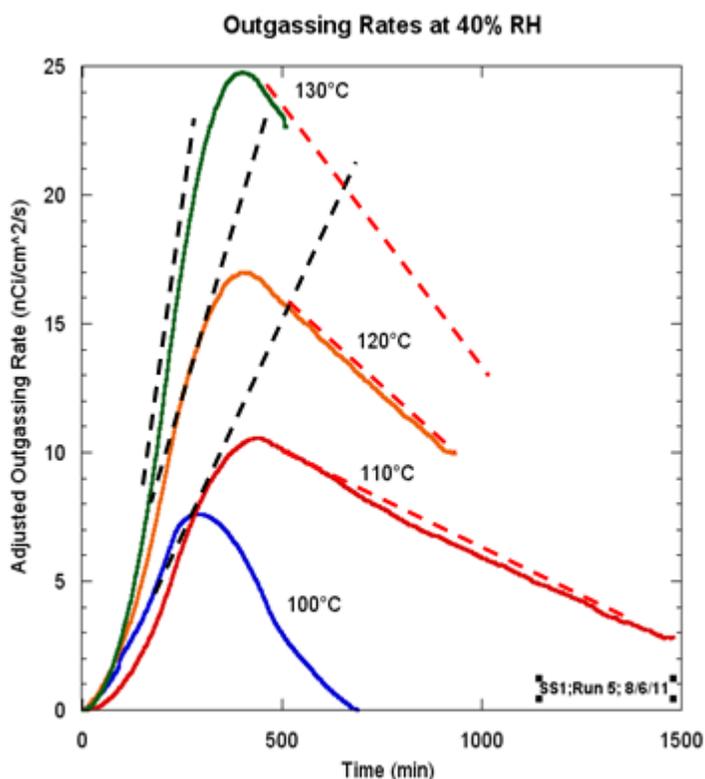


Fig 3: A plot of the supsmoothed outgassing rates at temperatures between 100 and 130°C at 40% relative humidity.

To compare the evolution of the curves for the three different temperatures, the individual curves were extracted from Figure 3, overlaid and plotted, such that the base of each peak was set to have an outgassing rate of zero. The results are shown in Fig. 4.



*Fig 4: The normalized outgassing rate peaks over time for various temperatures at 40% relative humidity. This is derived from Fig. 3 by plotting the peaks for each temperature by shifting each peak such that the base of all peaks occur at time zero and with outgassing rate zero. Also shown are the approximate tangent lines for each curve.*

This graph shows that the outgassing rate is dependent upon the temperature of the run. Not only does the peak outgassing rate increase with increased temperature, but the rate of the climb of the outgassing rate also increases (which can be seen from the tangent lines drawn along with the curves) with increasing temperature. Desorption is a thermally activated process.

The outgassing rate is observed to decline more rapidly after the peak with increasing temperature. This suggests that the store of water and tritium on the coupon surface participating in the desorption process is finite and dependent on the desorbing temperature.

The amount removed depends on the desorption temperature. The integral of the outgassing curves represents the quantity of water and tritium desorbed from the surface. The amount removed increases with increasing desorption temperature suggesting that a greater fraction of water and tritium bound to the surface is removed with increasing temperature.

Tritium residing in the metal bulk contributes negligibly to the quantity released from the surface. As tritium diffuses from a semi-infinite bulk to the surface, the tritium concentration profile in the metal will develop into an error function. The concentration at the oxide-metal interface will be a small value. The concentration deep in the bulk will be high. The maximum distance that a triton can travel at a given temperature and time will be given by:

$$\frac{z}{\sqrt{D * t}} = 1 \quad (2)$$

where  $z$  is the maximum penetration depth that a triton can propagate to in time  $t$  and  $D$  is the diffusivity of tritium in metal. Substituting  $1.2 * 10^{-9} \text{ cm}^2/\text{s}$  for a typical triton diffusivity<sup>(7)</sup> in copper at  $130^\circ\text{C}$  and  $30,000 \text{ s}$  (500 min), the typical duration of an experiment, suggests that tritons beyond a depth of 65 microns into the metal cannot contribute to the desorption process. At  $40^\circ\text{C}$ , the diffusivity decreases to  $1.3 * 10^{-11} \text{ cm}^2/\text{s}$  and tritons beyond a depth of 0.4 microns will not contribute to the amount desorbed. The amount of tritium dissolved in stainless steel is:

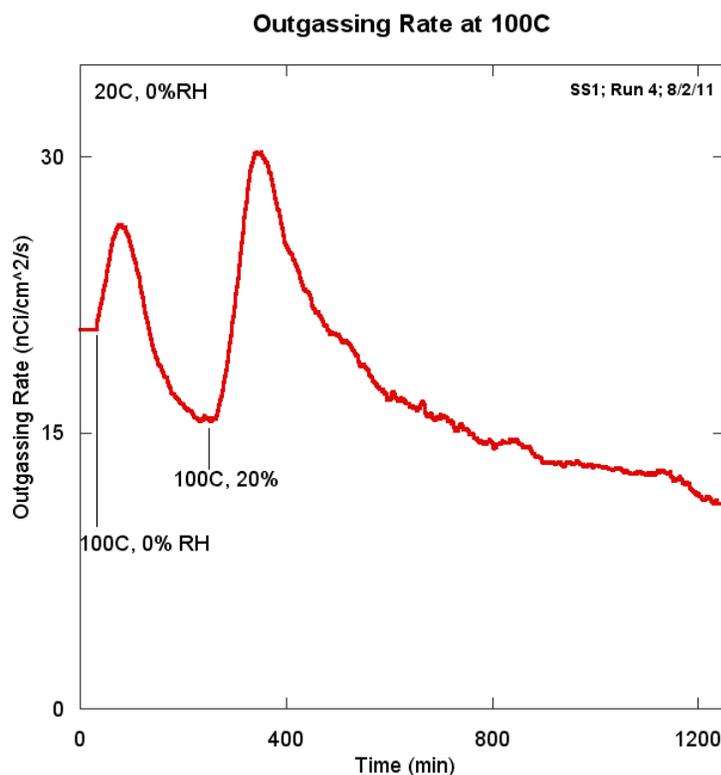
$$S = S_o \sqrt{P} \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

where  $S_o = 1.9$  scc of gas/cc of metal/atm<sup>1/2</sup> is a constant for hydrogen solubility in copper,  $P$  is the driving pressure used to charge the sample with tritium, 0.5 atm in this case, and  $E_a$  is the activation energy for dissolution of tritium in the metal, 9.1 kJ/mol<sup>(8)</sup>. At 40°C, the amount of tritium dissolved in 0.4 microns of copper will be 0.3 mCi. The total quantity of tritium collected in the 40°C run was 8 mCi. These calculations confirm that at temperatures below 130°C, tritium bound in the oxide layer dominates the desorption spectrum.

### **Dependence of Outgassing Rate on Humidity**

A run was conducted using a stainless steel coupon. The run was begun with a dry purge of helium at room temperature. After 30 minutes, the temperature of the coupon was increased to 100°C. At 314 minutes, the humidity of the dry gas stream was increased to 20%RH. The dry gas stream contained approximately 10 ppm water. At 20%RH the water content in the gas stream is 1000 ppm. The activity data collected was then run through a boxcar smoothing program and differentiated with respect to time. The boxcar-smoothed outgassing rates are shown in Fig 5.

Two peaks are seen in this run. One is for the experimental condition of 100°C and 0% RH; the other is at the same temperature for a relative humidity of 20%. To compare the evolution of the outgassing dependence on humidity, the individual curves were extracted from Figure 5 and plotted such that the starting point of both curves was set to the same value at time zero. The plot of the two overlaid curves is provided in Fig. 6.

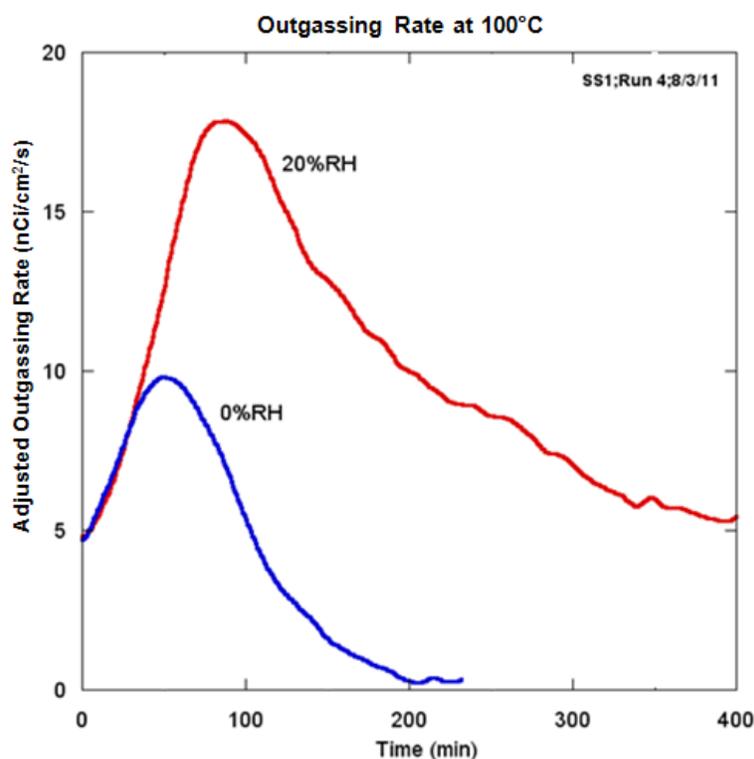


*Fig 5: A plot of outgassing rate over time at 100°C; the humidity of the gas stream was changed from 0 to 20% RH at 314 min.*

Figure 6 shows that outgassing rates for the two cases evolve in a similar manner, firstly increasing to a peak and then decreasing towards a steady state outgassing rate after a long time. This suggests that the rate-limiting step for desorbing tritium from the surface is determined by the arrival rate of water vapor to the surface. Tritium desorption from the sample decreases as the oxide layers closest to the gas stream are depleted of tritium. It appears that over the duration of the experiment, tritium located deep inside the oxide layer does not diffuse towards the surface rapidly and does not contribute to the emission.

The quantity of tritium removed increases in the presence of humidity. The quantity of tritium desorbed from the surface increased 216 fold when the humidity of the carrier increased

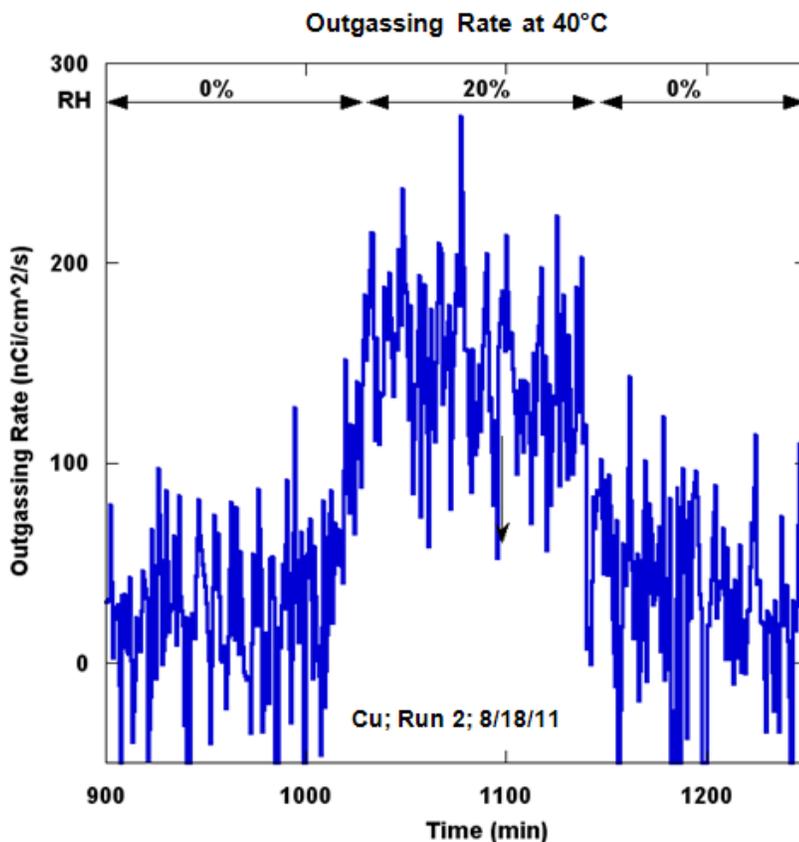
100 fold. This suggests that the number of monolayers contributing to the desorption process increased with the increase in humidity. It is also noteworthy that the duration of the outgassing process doubled, also suggesting that layers deeper in the oxide layer contributed to the emission.



*Fig 6: A plot of the normalized outgassing peaks over time for a run conducted at 100°C. The outgassing profiles for the runs at both humidities were adjusted to coincide at time zero to highlight the similarities and differences in the two profiles.*

A second test was conducted to investigate the outgassing rate dependence on humidity at 40°C. The humidity of the gas stream was changed to 20% RH and a resultant increase in the outgassing rate is shown. Fig. 7 shows the boxcar-smoothed outgassing rates of this experiment. The average outgassing rate into the dry stream is about 20 nCi/cm<sup>2</sup>/s. When the humidity is increased to 20%RH, the average outgassing rate increases to about 150 nCi/cm<sup>2</sup>/s. Returning to

dry purge stream conditions causes the outgassing rate to return to its previous level of about 20 nCi/cm<sup>2</sup>/s. This figure illustrates that humidity in the purge stream stimulates desorption from the copper surface.



*Fig 7: A plot of outgassing rate over time conducted at 40°C. The outgassing rate increases with increased humidity*

At 40°C, a 100 fold increase in water content in the purge stream resulted in an 8 fold increase in the outgassing rate. As discussed in the 100°C run, the number of monolayers participating in the desorption process increases with increased humidity. However, the total number of layers involved appears to decrease as the metal temperature decreases. The

assumption in both the 40 and 100°C runs is that tritium is uniformly distributed throughout the layers of oxide from the gas/oxide interface through to the oxide/metal interface.

## Conclusions

Experiments have been conducted to measure the tritium outgassing rate from stainless steel and copper coupons. The outgassing rate is seen to depend on both the temperature of the metal and on the humidity of the purge stream. Increasing the metal temperature increases the outgassing rate from the surface. Increasing the humidity of the gas stream also increases the outgassing rate.

Increasing either the temperature or the humidity appears to increase the number of oxide monolayers that participate in the release of tritium. At temperatures below 130°C, tritium dissolved in the metal bulk does not contribute to the outgassing profile.

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