

# On Predicting Transient Pressure in Vacuum Systems Featuring Getter Materials

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# Introduction

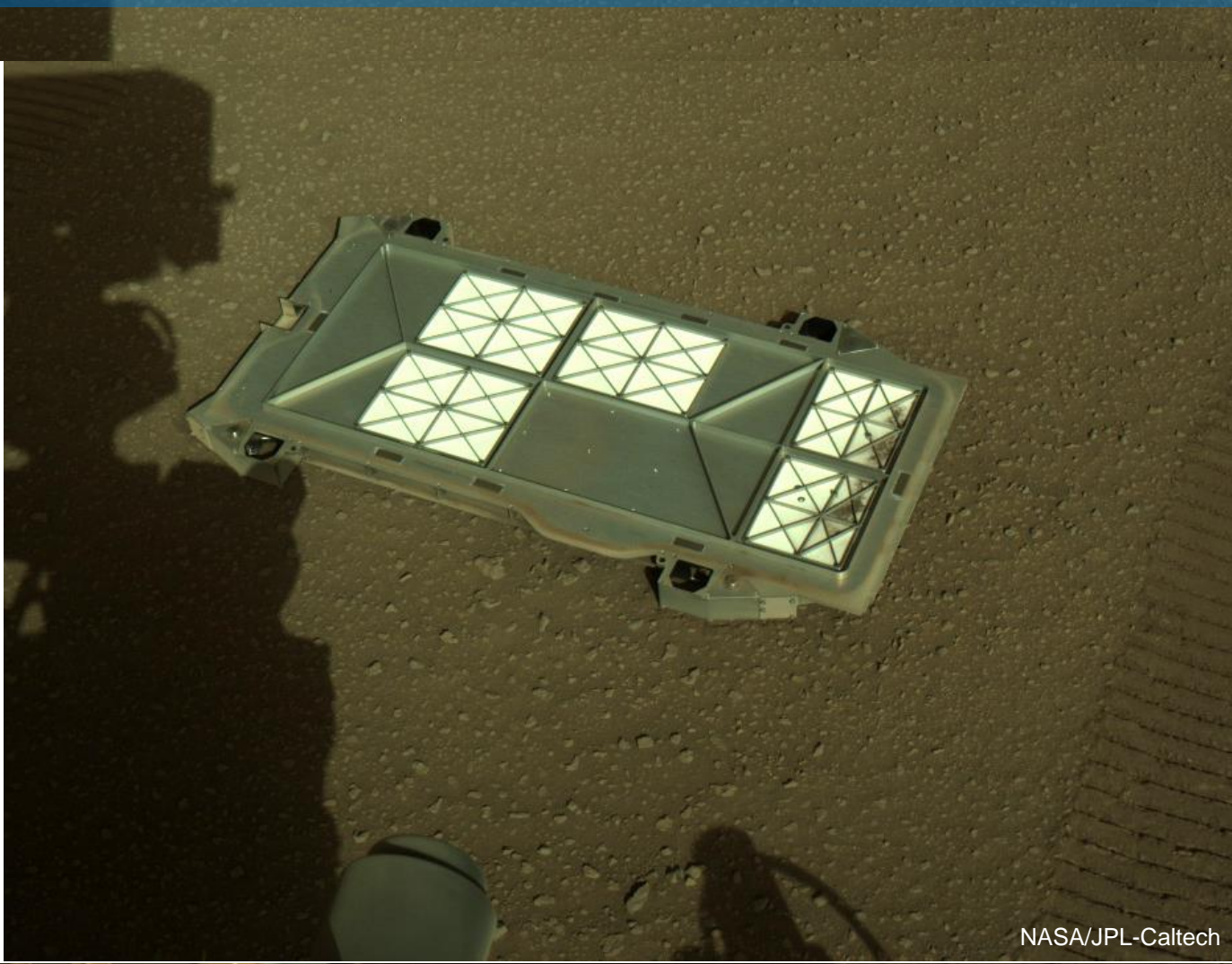
- **Getter materials consisting of metal alloys, molecular adsorber coating (MAC) zeolite materials, and organic polymers have been employed in several spaceflight applications to scavenge unwanted gases under vacuum**
  - HST Wide Field Planetary Camera-2 (WFPC-2)
  - JWST/OTIS thermal vacuum (TV) testing in NASA JSC's Chamber A
  - Mars Perseverance Rover Sample Caching System while in transit
- **Some missions are using or considering getters to maintain low internal pressure levels**
  - Mars Insight Lander, SEIS instrument
- **Often, the capacity of getter material used in such applications is determined by matching or exceeding an estimate of the amount of a particular target gas species anticipated to be produced in a system by the end of a mission's operational period**
  - insufficient for predicting transient pressure or species partial pressure/molecular flux since both molecular source rates and getter effectiveness are diminishing independently from one another

# JWST Thermal Vacuum Testing—MAC Panels



NASA Goddard/Chris Gunn

# Mars Perseverance Rover Example—Tenax®



NASA/JPL-Caltech

# Objective

- **Develop analytical tools to describe general sorbing material influence on QCM rates when both outgassing rates (OGRs) and panel effectiveness decay with time**
  - Work with gas loads  $Q$  and partial pressures  $p$
- **Develop solutions for various cases of increasing complexity**
  - Outgassing, no pumping, sorbing material collecting at maximum performance
    - “High Immersion Rate (HIR) Limit”
  - Same, but with pumping present
  - Same, but with pumping present and sorbing material collecting below HIR limit
- **Results lead to the observation that for a given system there can be a critical pressure defining when the HIR limit has been reached**

# Development Focus

- **Attention focused on spaceflight high vacuum (HV) rather than ultrahigh or extremely high vacuum (UHV or XHV) environments**
  - UHV & XHV attention tends to focus on removal of H<sub>2</sub> and CO from small, simple, metallic systems that may be heated > 150 °C for days
  - Spaceflight systems in HV environment will mostly encounter water vapor and volatile condensable materials (VCMs) from a variety of sources
    - cannot tolerate temperatures nearly as high as UHV and XHV systems

# Mass Conservation Statement

- Assume spatially-averaged, uniformed properties in thermal vacuum chambers or sealed, evacuated vessels in the presence of outgassing sources, pumping, and a sorptive material

$$\frac{d}{dt} \iiint \rho dV = V \frac{d\rho}{dt} = \dot{m}_{gen} - \dot{m}_{pump} - \dot{m}_{sorb}$$

- Describe solutions in terms of pressure or partial pressure
  - Assume mass conservation statement may written in terms of gas load

$$V \frac{dp}{dt} = \dot{m}_{gen} RT - \dot{m}_{pump} RT - \dot{m}_{sorb} RT = Q_{gen} - Q_{pump} - Q_{sorb}$$

- Mass flux impingement related to pressure by Hertz-Knudsen equation

$$\dot{\phi} = \frac{p}{\sqrt{2\pi RT}}$$

# Outgassing Sources

- Often acceptable to assume  $\dot{m}_{gen}$  may be described by classical, one-dimensional, diffusion-limited outgassing from a sheet of material, thickness  $L$  with exposed area  $A$  as the solution to Fick's Second Law

$$\dot{m}_{gen}(\text{classical}) = \dot{\phi}A = \Delta c_0 A \sqrt{\frac{v}{\pi t}} \left[ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \left( \exp \left[ -\frac{n^2 L^2}{vt} \right] \right) \right] \approx \Delta c_0 A \sqrt{\frac{v}{\pi t}}$$

- Testing experience indicates depletion of a material's centerline driving potential does not occur, can ignore finite thickness effects
- More generally, one must contend with measurement data that is best fit empirically with

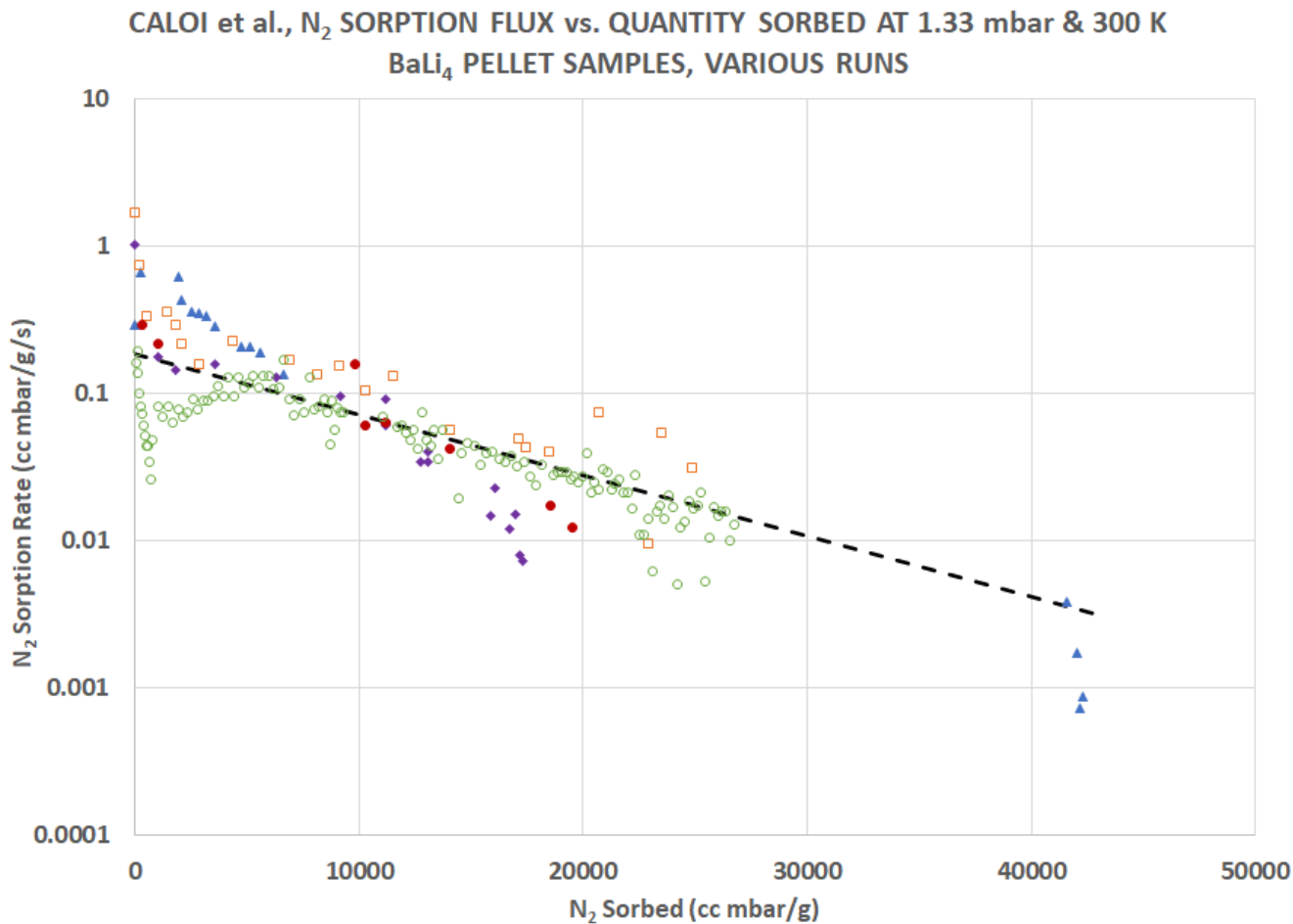
$$\dot{m}_{gen}(\text{non-classical}) = \frac{bA}{t^\eta}$$

- Surface desorption of moisture from metallic surfaces tends to follow  $\eta = 1$
- For atmospheric leaks into HV,  $\eta = 0$

# Pumping & Sorption

- **Pumping gas load is a product of vessel pressure  $p$  and effective pumping speed  $S_{eff}$** 
  - Under FM, equilibrium conditions,  $S_{eff} = A_{p,eff} \sqrt{RT/2\pi} = \text{constant}$
- **Getter material sorption effectiveness often seeks to establish how much gas may be sorbed for a given mass of surface area of material**
  - Results usually displayed in some sort of phase portrait diagram
    - Sorption rate plotted against amount already sorbed
    - When rate is relatively low compared to initial measurement, this becomes an indication that sorption capacity is being approached
  - This information is not directly useful for determining the evolution of pressure within a HV system
    - Need information as a function of time
  - Example case follows

# Phase Portrait Diagram Example



# Sorption Gas Load—High Infusion Rate (HIR) Limit

- The collection rate of this getter in an excess N<sub>2</sub> environment is pretty-well fitted by

$$\frac{Q}{Q_{ref}} = \frac{\dot{m}}{\dot{m}_{ref}} = \exp\left(-\frac{m}{m_{ref}}\right)$$

– It may happen that other sorbing systems will exhibit different characteristics

- For mass collection rate, cumulative mass as functions of time, solving for  $m(t)$ :

$$m(t) = m_{ref} \ln\left(1 + \frac{\dot{m}_{ref} t}{m_{ref}}\right) = m_{ref} \ln\left(1 + \frac{t}{t_{ref}}\right)$$

- Getter pumping gas load  $Q_g$  becomes

$$Q_{g,HIR} = \dot{m}_{g,HIR} RT = \frac{t_{ref}}{t + t_{ref}} \dot{m}_{ref} RT$$

# Pressure w/ OGR & Getter, No Pumping, HIR Limit

Assume period begins right after getter activation

$$V \frac{dp}{dt} = Q_{in} - Q_{g,HIR}$$

Pressure solution becomes

$$p(t) = p_0 + \frac{bART}{V(1-\eta)} t^{1-\eta} - \frac{m_{ref}RT}{V} \ln\left(1 + \frac{t}{t_{ref}}\right) \quad (\eta \neq 1)$$

- Solution indicates getter's presence reduces the pressure increase independent of the outgassing source since it is collecting at its maximum rate
- If enough sorbing material is present such that  $p(t)$  decreases with time, it will violate the HIR limit before approaching zero
- Of course it will never reach zero because gas has to be emitted before it can be sorbed!

# Pressure w/ OGR, Getter, & Pumping, HIR Limit

- Add gas load associated with pumping

$$V \frac{dp}{dt} = Q_{in} - Q_p - Q_{g,HIR}$$

- Let  $\tau \equiv (V/A_{p,eff})\sqrt{2\pi/RT}$ ,  $s \equiv t/\tau$

$$p(t) = p_0 e^{-s} + \frac{bART}{V} \tau^{1-\eta} \left( e^{-s} \int_0^s \frac{e^s}{s^\eta} ds \right) - \frac{m_{ref}RT}{V} e^{-(s+\xi)} \int_\xi^u e^{e^u} du \quad (\eta \neq 1)$$

- A function solving the first integral was described in NASA/CR 2018-219028

- For  $\eta = 1/2$  it is given by Dawson's Integral  $D(x)$  where  $x \equiv \sqrt{s}$
- More generally for  $\eta$ , as  $t \gg \tau$ , the expression relaxes to

$$\frac{bART}{V} \tau^{1-\eta} \left( e^{-s} \int_0^s \frac{e^s}{s^\eta} ds \right) \rightarrow \frac{bART}{S_{eff} t^\eta} = \frac{\dot{m}_{gen}RT}{S_{eff}} \quad (s \rightarrow \infty)$$

# Pressure w/ OGR, Getter, & Pumping, HIR Limit

$$p(t) = p_0 e^{-s} + \frac{bART}{V} \tau^{1-\eta} \left( e^{-s} \int_0^s \frac{e^s}{s^\eta} ds \right) - \frac{m_{ref} RT}{V} e^{-(s+\xi)} \int_\xi^u e^{e^u} du \quad (\eta \neq 1)$$

- When  $\eta = 1$ , the first integral may be solved by the exponential integral  $Ei(-s)$

$$\frac{bART}{V} \left( e^{-s} \int_0^s \frac{e^s}{s} ds \right) = -e^{-s} \frac{bART}{V} Ei(-s) \rightarrow \frac{bART}{V} \frac{\tau}{t} = \frac{\dot{m}_{gen} RT}{S_{eff}} \quad (s \rightarrow \infty)$$

- The second integral is also related to the exponential integral  $Ei(-e^u)$ , with

$$u \equiv \ln\left(\frac{t+t_{ref}}{\tau}\right) \quad \text{and} \quad \xi \equiv \ln\left(\frac{t_{ref}}{\tau}\right)$$

# Getter Gas Load—General (Below HIR Limit)

- In general, getter sorption performance may be limited by the rate at which a target gas encounters the getter surface
- Rate at which that impinging gas is newly sorbed also depends on the getter's sorption history
  - Can describe as an evolving effective area
- In terms of gas load

$$Q_{sorb}(t) = \dot{m}_{sorb} RT = p(t) A_{sorb}(t) \sqrt{\frac{RT}{2\pi}}$$

– where

$$A_{sorb}(t) = A_{ref} \exp\left(-\frac{m(t)}{m_{ref}}\right) \quad \text{and} \quad m(t) = \int_0^t \dot{m}(t) dt = \int_0^t \frac{Q_{sorb}(t)}{RT} dt$$

# Getter Gas Load—General (Below HIR Limit)

- For an evacuated vessel with an outgassing source undergoing pumping and sorption

$$\frac{dp}{dt} = \frac{bART}{Vt^\eta} - \frac{p}{\tau} \left[ 1 + \frac{A_{sorb,ref}}{A_{p,eff}} \exp \left( \frac{-1}{m_{ref}RT} \int_0^t Q_{sorb}(t) dt \right) \right]$$

- The second bracketed term indicates how the presence of a getter modifies the influence of pumping
  - The loading history integrand is also a function of pressure, so it appears one must resort to numerical quadrature to solve for pressure
- When exposed to enough gas, eventually sorptive capacity will diminish such that performance will degenerate to HIR limit behavior as total capacity is reached even if it started out operating well below that limit

# Critical Sorption Pressure

- Returning to the general expression for sorption gas load

$$Q_{sorb}(t) = \dot{m}_{sorb}RT = p(t)A_{sorb}(t)\sqrt{\frac{RT}{2\pi}}; \quad A_{sorb}(t) = A_{ref} \exp\left(-\frac{m(t)}{m_{ref}}\right)$$

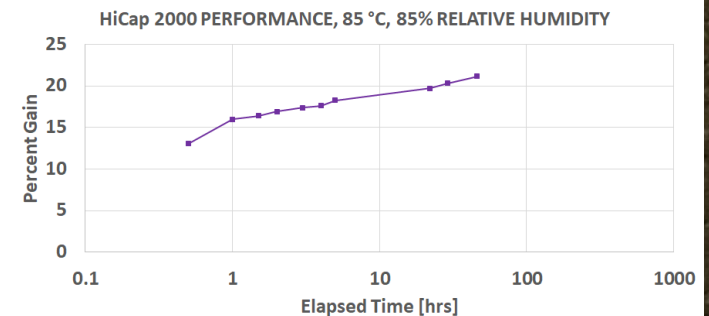
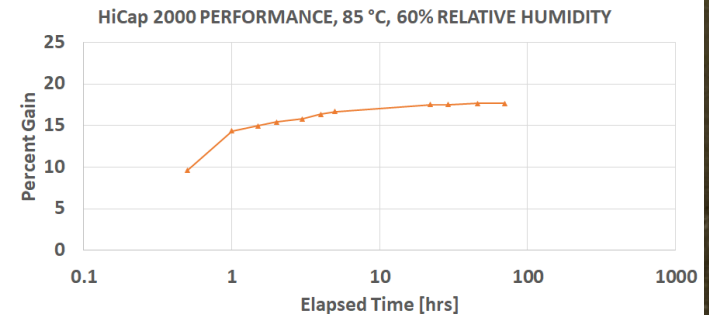
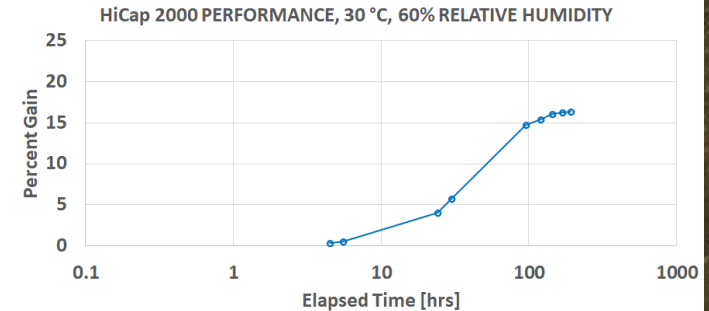
- Normalization factor  $A_{ref}$  associated with minimum pressure  $p_{sorb,crit}$  that produces  $\dot{m}_{ref}$  in the HIR limit

$$\dot{m}_{ref} \sqrt{2\pi RT} = p_{sorb,crit} A_{ref}$$

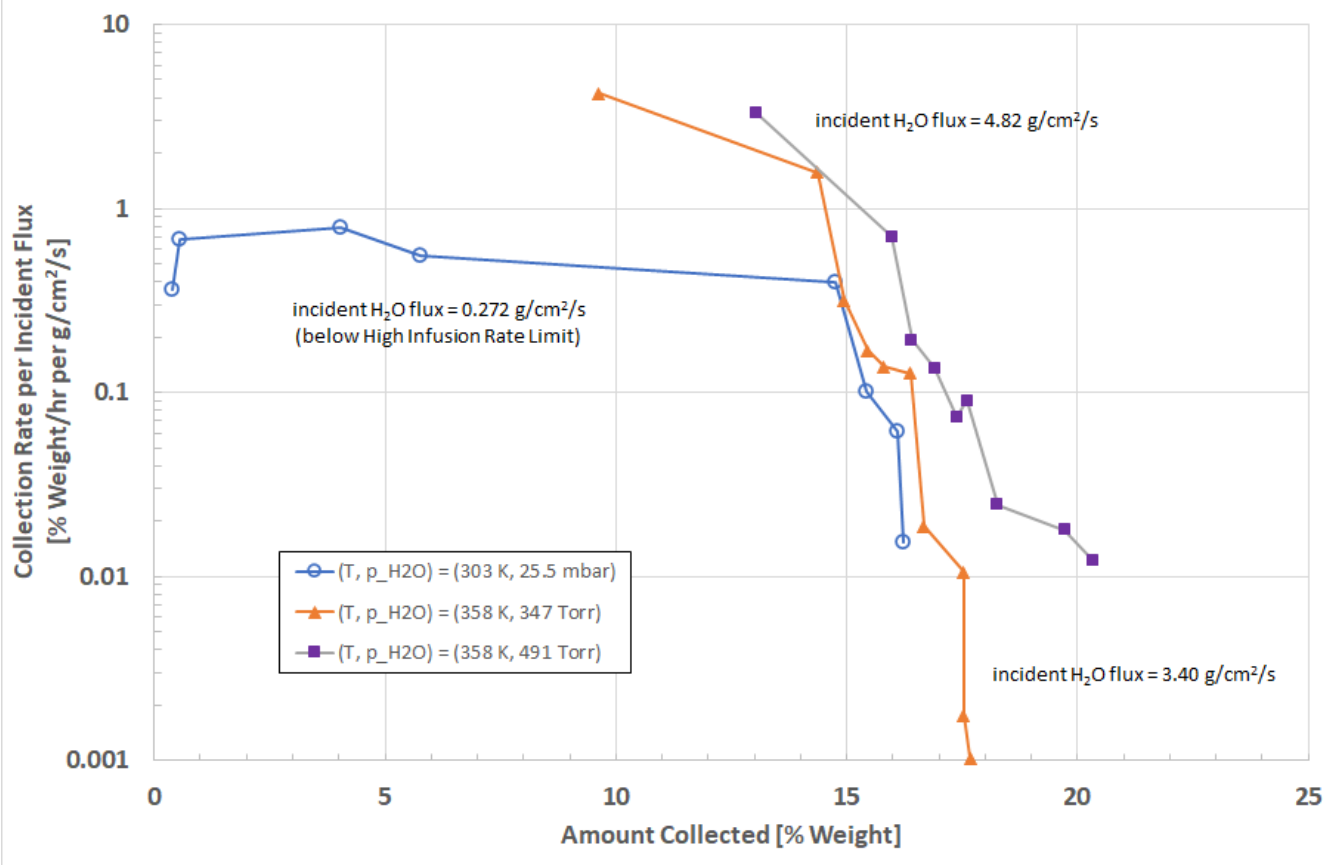
- Reference area is associated with a given physical vacuum system configuration, while the critical pressure is a getter property that appears to be independent of that configuration
  - As first approximation, perhaps assume  $A_{ref}$  equals projected getter area presented to the vessel cavity

# Critical Sorption Pressure Example

- **StayDry® HiCap™ 2000 High Capacity Moisture Getter** is an organic polymer used in various semiconductor, optical, electronic, and MEMS-related applications
- The technical data sheet describes how well it collects moisture in a variety of temperature and relative humidity conditions in air
  - Sorption versus time!
- **Create a sort of phase portrait plot from this data**
  - Based on average conditions
- **Seems to cross into HIR limit with**
  - $26 \text{ mbar} \leq p_{\text{crit}} \leq 347 \text{ mbar}$



**DAVINCI--StayDry HiCap2000 PASTE MEASUREMENTS, PHASE PLOT**  
 based on transient collected mass data, marketing sheet, irregular time intervals



# Concluding Remarks

- **The addition of sorptive materials to evacuated systems requires awareness of which species need removal along with their magnitudes, however phase portrait diagrams are insufficient to predict transient system performance**
  - Measurements of sorbing material performance tend to occur in the HIR limit in part to determine their collecting capacity
- **A framework has been presented for overcoming this omission by integrating a curve fitted to data in the HIR limit to describe transient performance in terms of sorbed mass and collection rate**
  - Spatially-averaged solutions for transient pressure were developed for a number of relevant physical configurations above and below the HIR limit
- **Sub-HIR limit behavior suggests existence of a critical pressure parameter that heralds the onset of the HIR limit for a sorbing material that appears to have been generally overlooked**

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