Traceable outgassing measurements at NIST: ultra-low outgassing rates and new materials

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Vacuum Project: Outgassing Measurements

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All data and materials presented in this talk are preliminary

Please, no copies or pictures

Thanks!

Outgassing Measurements at NIST

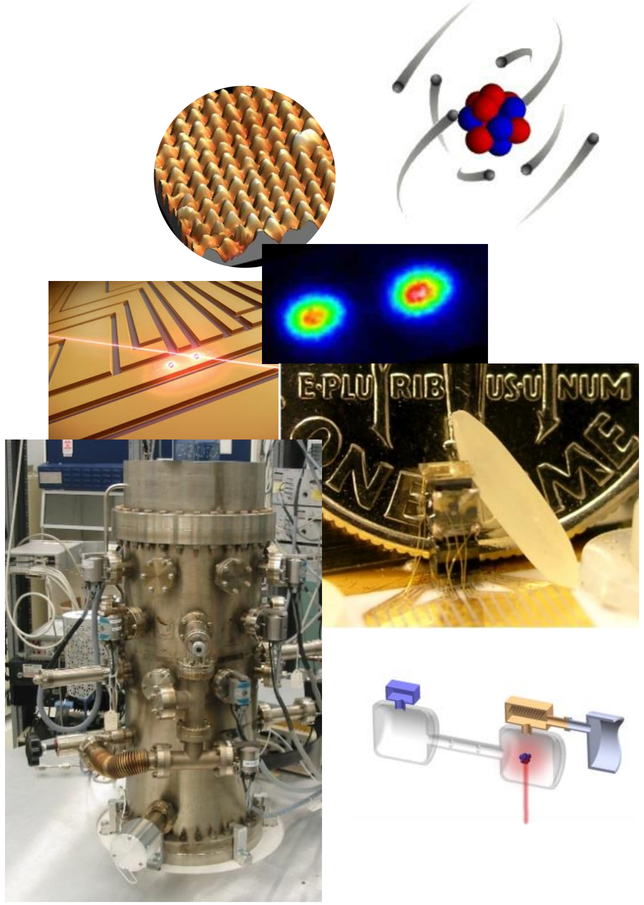
Motivation:

- Support NIST projects
  - Creating UHV and XHV standards
  - Atomic/quantum physics research
  - New Materials for Sensors

- External requests for outgassing measurements

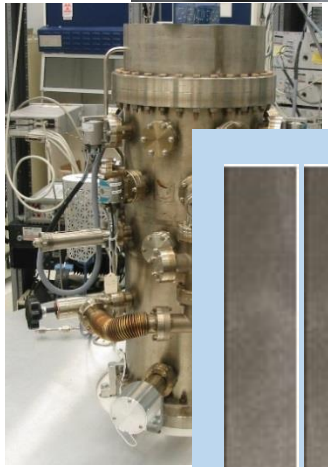
=> Not a standard calibration service

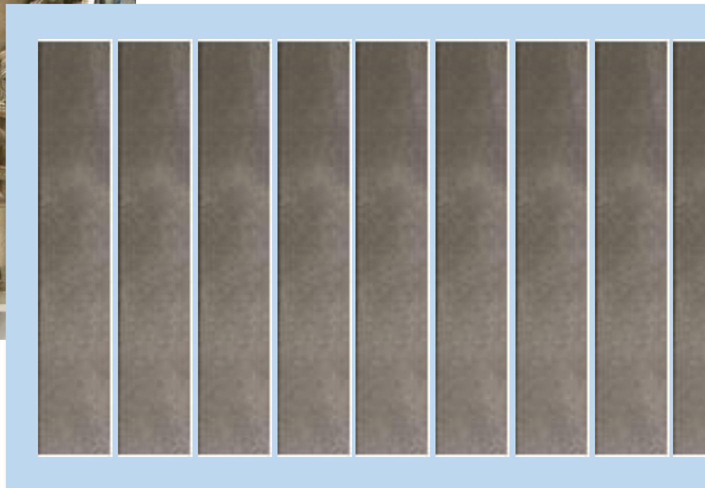
=> Research & Development



Outgassing Measurements at NIST

- Test Chambers and components
    - Different heat treatments, processes
    - Different metals
        - Stainless steel, Titanium, Aluminum
    - New materials
        - 3D printed
- Real chambers
    - Need to know outgassing rates
- Sample Materials (Coupons)
    - In vacuum use
        - Wires, Metals, Epoxies, etc.
    - Sensors or gas storage
        - Polymers, 3D printed materials

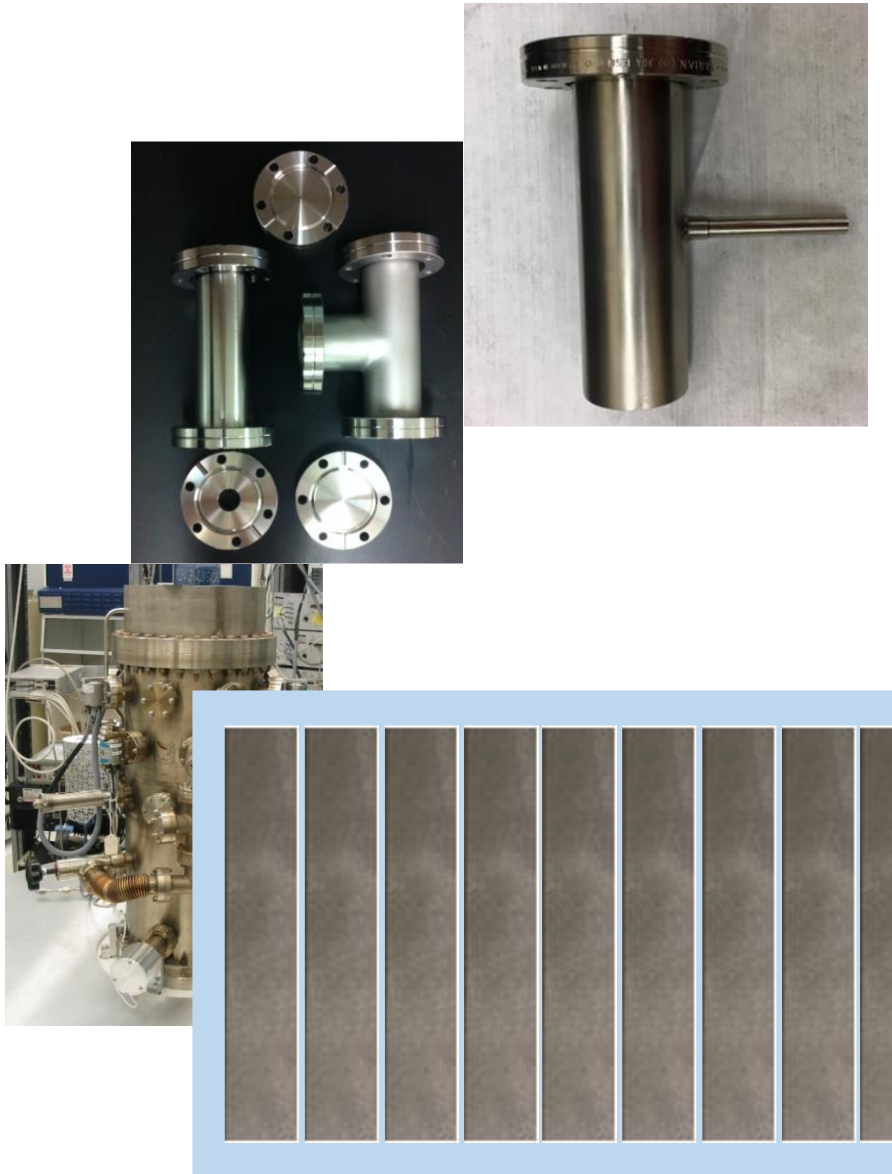




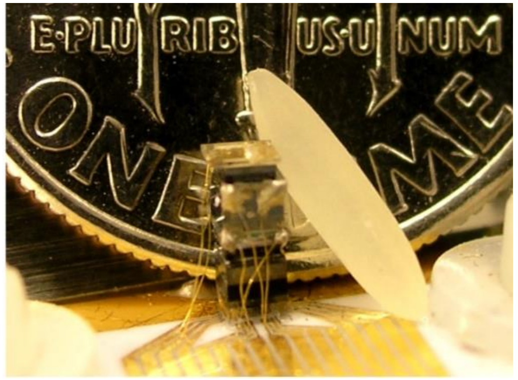
Outline

- Test Chambers and Components
- Real chambers
- Sample Materials (Coupons)

- Comments on Working Draft ISO/PDTS 20177.5 Procedures to measure and report outgassing rates



What quantities are useful?



- Total Outgassing Gas Flow: Pa·L·s^{-1}
  - Useful testing specific component to be used in vacuum
  - Not useful for general class of components

- **Total Outgassing Gas Rate: Pa·L·s^{-1}· cm^{-2}**
  - Useful for engineering vacuum systems and experiments
  - Area may be hard to measure
  - Nominal geometric surface area OK for most engineering purposes
    - Assumes reproducible area

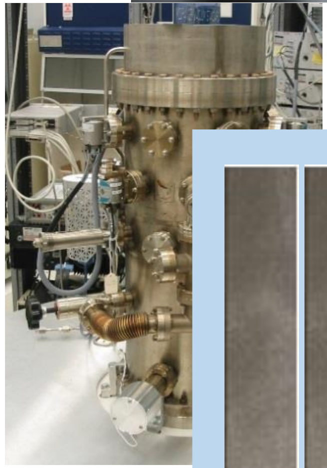
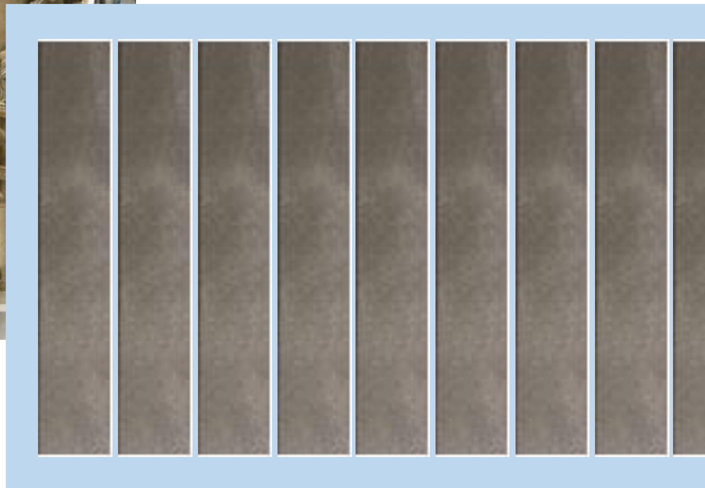
Most useful for our purposes

- More or less consistent with section 1
  - Q (Pa·L·s^{-1}· cm^{-2}) is not defined in section 4, but is widely used and very useful.

Outline

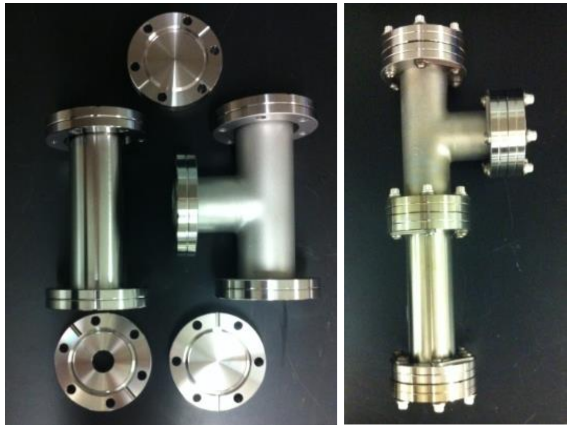
- **Test Chambers and Components**
- Real chambers
- Sample Materials (Coupons)
- Comments on Working Draft ISO/PDTS 20177.5 Procedures to measure and report outgassing rates



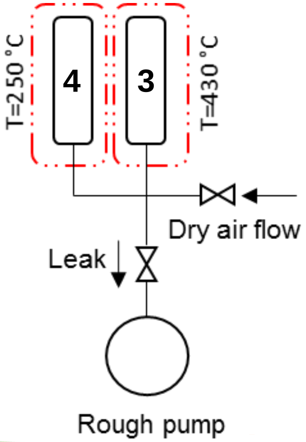



Test Chambers and Components:
400 °C Vacuum Bake Vs. Air Bake Study

Samples



- Identical commercial chambers
- Sample 1 baked in vacuum 430 °C, 15 days
- Sample 2 baked in air 430 °C, 15 days

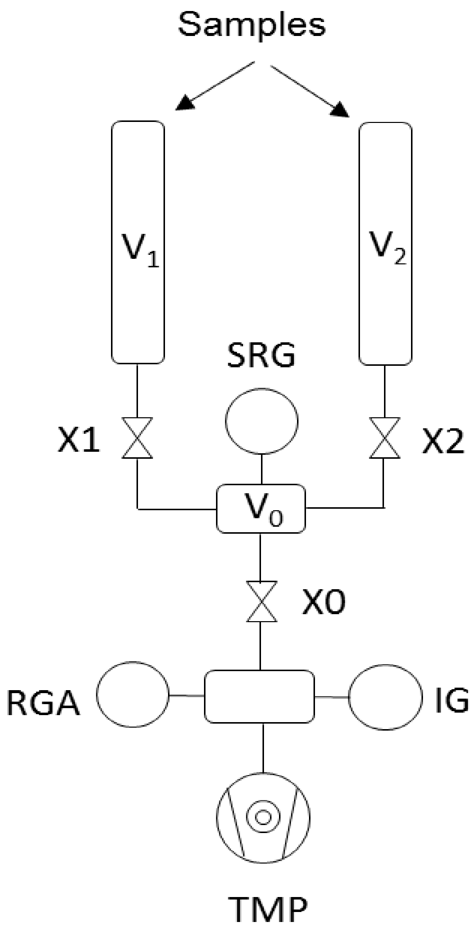


Baking history of sample chambers

Sample	Treatments	Bake temperature	Bake time
		(°C)	(h)
1	Vacuum bake	430	360
2	Air bake	430	360
3	Dry air bake	430	48
4	Dry air bake	250	48
1'	Dry air bake	430	24

Test Chambers and Components:

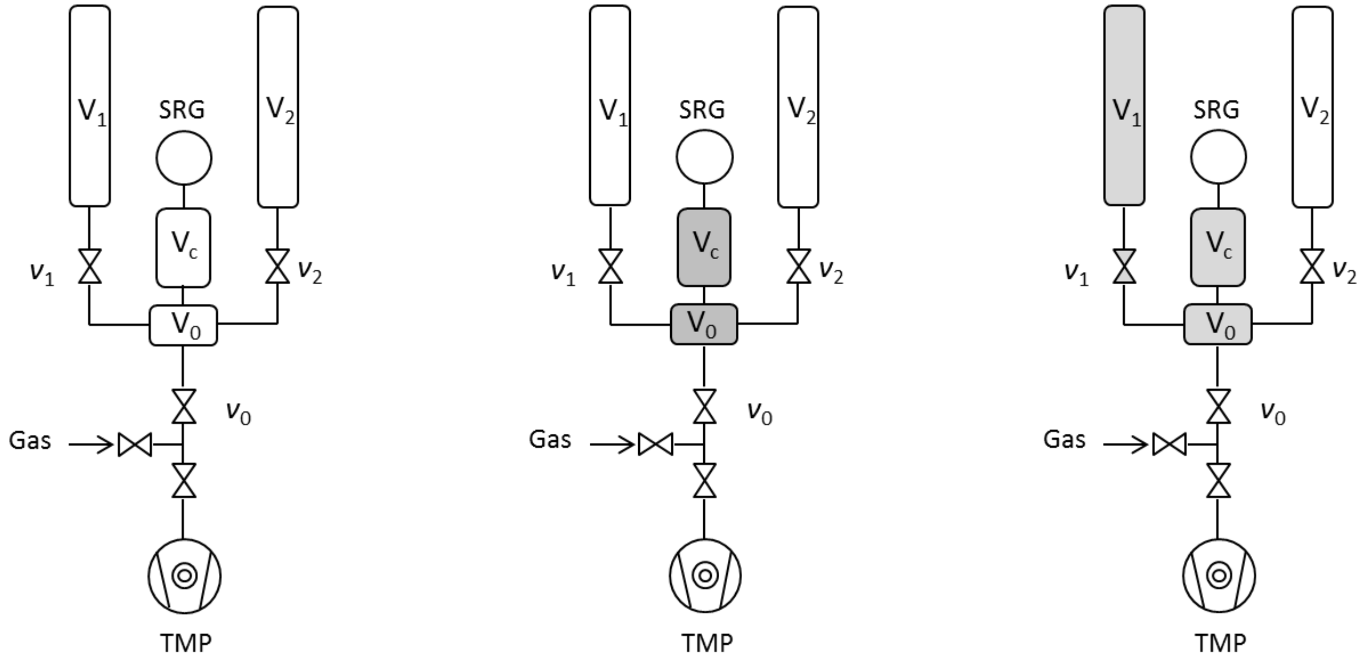
400 °C Vacuum Bake Vs. Air Bake



- Section 5.3 Accumulation System
  - (Rate-of-Rise)
- N_2 Calibrated SRG
  - H_2 accommodation coefficient differs from N_2 (within 3%)
- Samples baked at 150 °C before measurements
  - Baking will shift calibration factor

Volume Calibration:
Step 1-add reference volume

Static expansion method

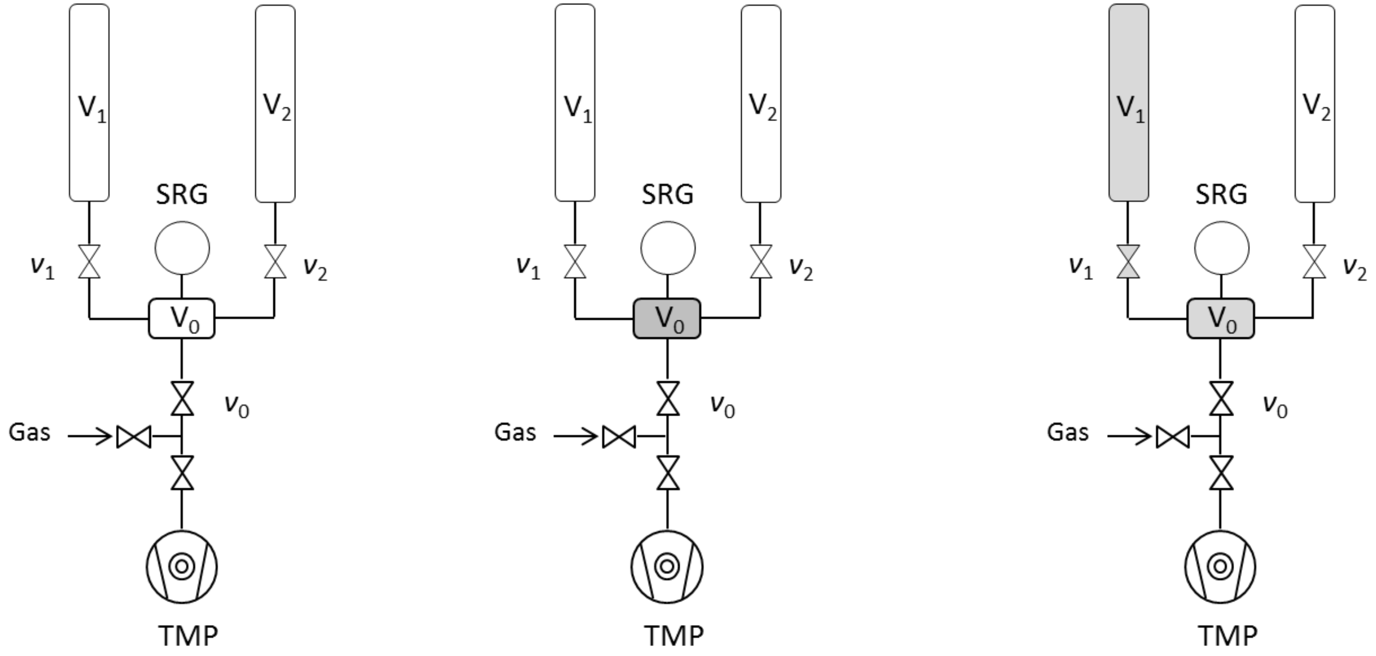


$$p_0(V_0 + V_c) = p(V_0 + V_c + V_1)$$

Volume Calibration:

Step 2-no reference volume

Static expansion method



$$p_0(V_0 + V_c) = p(V_0 + V_c + V_1)$$

$$p'_0 V_0 = p'(V_0 + V_1)$$

$$V_0 = \frac{1 - R}{R - R'} \times V_c$$

$$V_1 = (R' - 1) \times V_0$$

Chamber	Volume (L)
V_c	0.118
V_0	0.091
$V_1 = V_2$	0.291

Uncertainty Budget

400 °C Vacuum Bake Vs. Air Bake

$$q_0 = Q_0 A_0 = V_0 \frac{dp_0}{dt} \qquad Q_1 = \frac{1}{A_1}\left(\left(V_0 + V_1\right) \frac{dp_{01}}{dt} - q_0 \right)$$

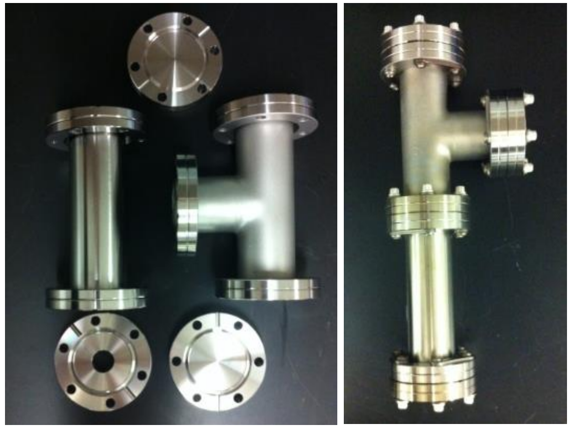
SRG pressure uncertainty	
Component	**Relative Uncertainty of *p* (percent; *k*=2)**
Accommodation Coefficient (N_2)	0.5
H_2 Accommodation Coefficient (change from N_2)	6%
Change from 150 C bake	2%
Calibration Stability	2%
TOTAL	7%

Section 7 doesn't specifically address this type of Basic accumulation system (5.3.1)

TOTAL UNCERTAINTY BUDGET		
Component		**Relative Uncertainty of Q_1 (percent; *k*=2)**
Area	A_1	0.1
Reference Volume	V_0	2
Chamber Volume	V_1	2
Pressure Rise	$\frac{dp}{dt}$	7
Background flow	q_0	7
Type A (Long-term repeatability)		19
TOTAL		22

Test Chambers and Components:
400 °C Vacuum Bake Vs. Air Bake Study

- Outgassing of chambers still requires background subtraction
- This type of accumulation system not specifically addressed
- The background outgassing of gauges (SRG), valves, etc. must be taken into account.
- Long term stability dominates uncertainty
- We require H_2 outgassing rates
  - Baked systems, little to no N_2 outgassing
  - Differ by nearly factor of 4



Sample	Treatments	Bake temperature	Bake time	N_2 Equivalent Outgassing rate	H_2 Outgassing rate
		(°C)	(h)	(Pa l s^{-1} cm^{-2})	(Pa l s^{-1} cm^{-2})
1	**Vacuum bake**	**430**	**360**	1.8×10^{-9}	4.7×10^{-10}
2	**Air bake**	**430**	**360**	1.8×10^{-9}	4.8×10^{-10}
3	Dry air bake	415	48	1.9×10^{-11}	5.1×10^{-12}
4	Dry air bake	250	48	1.3×10^{-10}	3.4×10^{-11}
1‘	Dry air bake	430	24	3.8×10^{-10}	1.0×10^{-11}

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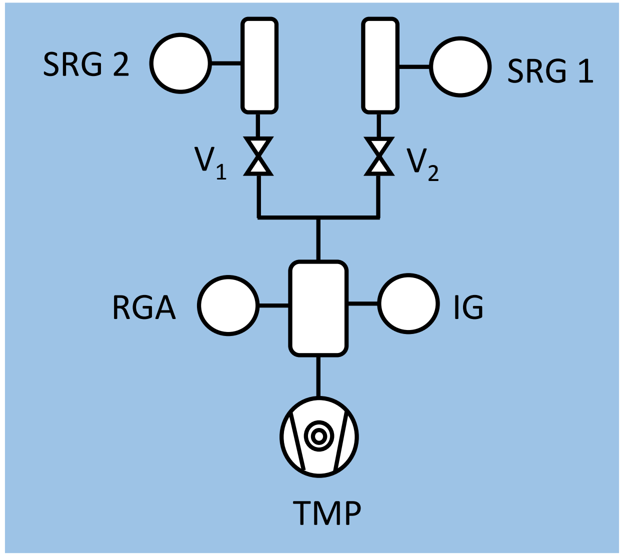
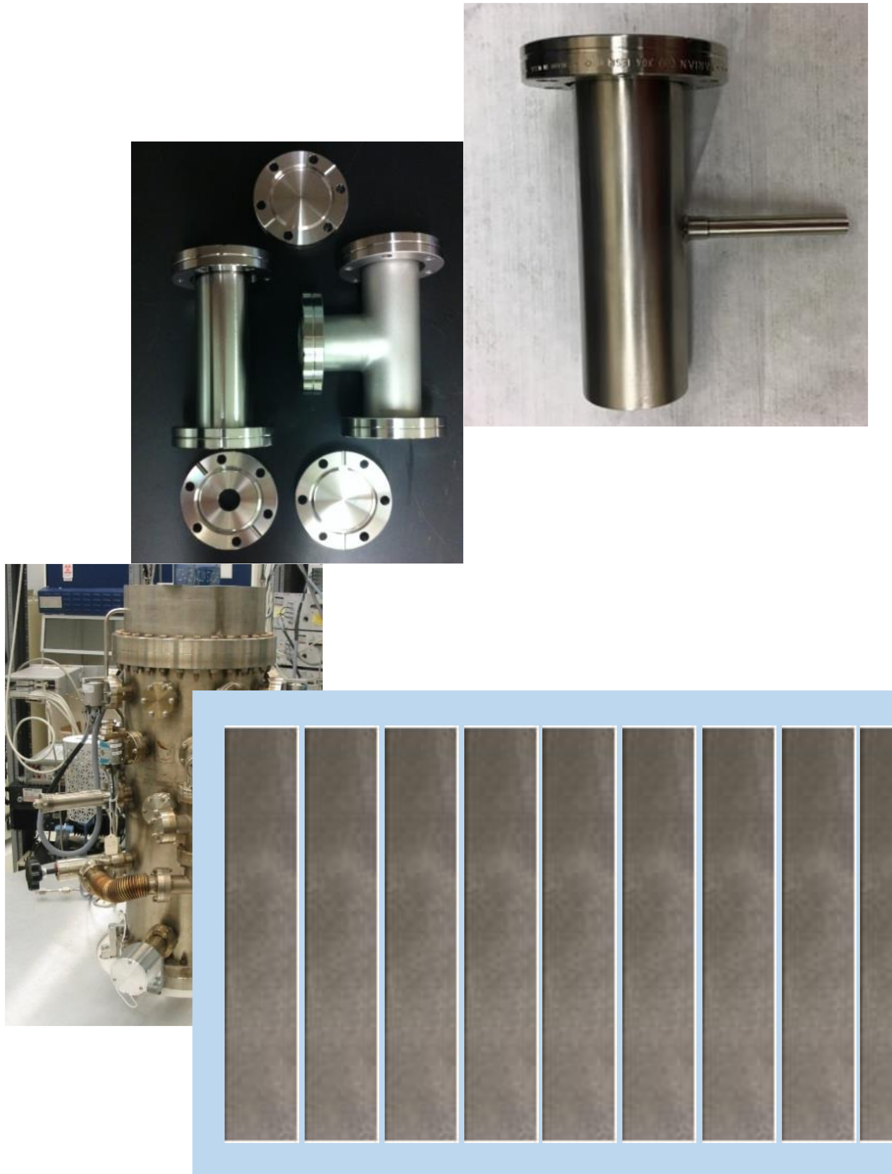
Test Chambers and Components:
Special Sample Chambers

- SRG is incorporated into sample chamber
  - Thimble is same material/treatment
- Still have background outgassing due to valve.
- We are interested in:
  - H_2 outgassing after 150 °C bake
  - H_2O pumpdown curve before bake
  - **NOT** N_2 equivalent



Outline

- Test Chambers and Components
- **Real chambers**
- Sample Materials (Coupons)
- Comments on Working Draft ISO/PDTS 20177.5 Procedures to measure and report outgassing rates



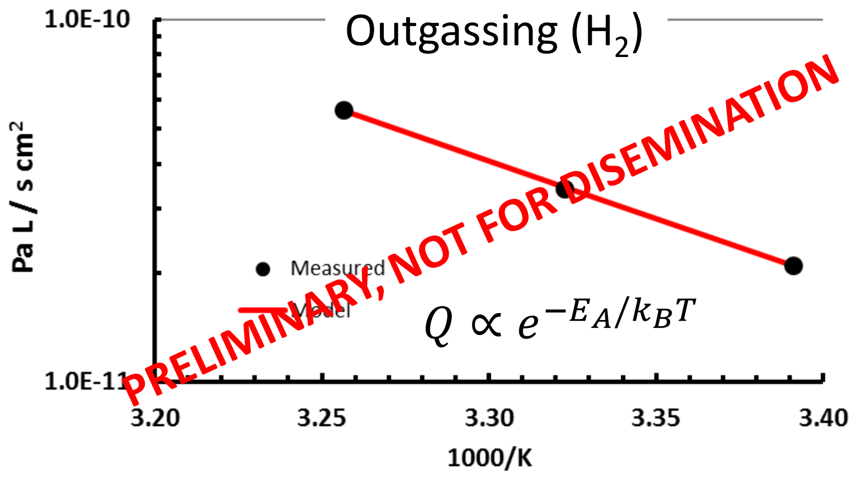
Real Chambers:

XHV Chamber at NIST

Wall thickness:
0.125” (3.2 mm)

Dome thickness :
0.25” (6.4 mm)

Vacuum Fired 850 °C, 2 hrs



H_2 OG RATE:
2 X 10^{-11} Pa L/cm²/s

All Rotatable Flanges

Vacuum Fired 950 °C, 2 hrs

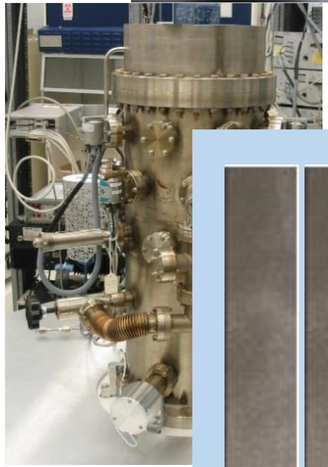
Real Chambers:
XHV Chamber at NIST

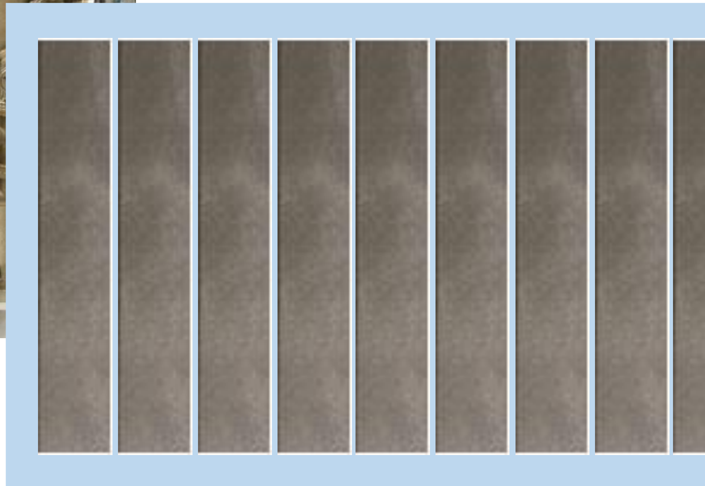
- The background outgassing rate of gauges, valves, etc. may have to be considered
- H_2 outgassing rate is required, not N_2 equivalent
- Temperature dependence may be important
  - >10%/K
  - ISO document says 23±7 °C, should not change by more than 2 °C during measurement (6)



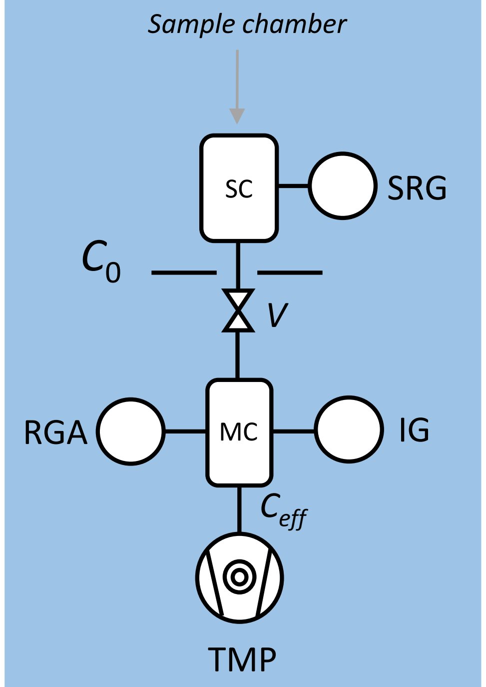
Outline

- Test Chambers and Components
- Real chambers
- **Sample Materials (Coupons)**
- Comments on Working Draft ISO/PDTS 20177.5 Procedures to measure and report outgassing rates





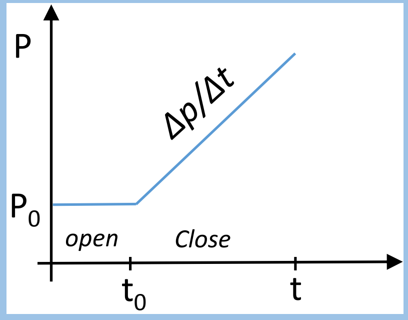
Sample Materials (coupons):
Measurement System 1



- **Rate-of-rise (Accumulation 5.3)**

$$q_{out} = V_{sc} \times \frac{\Delta p_{SC}}{\Delta t}$$

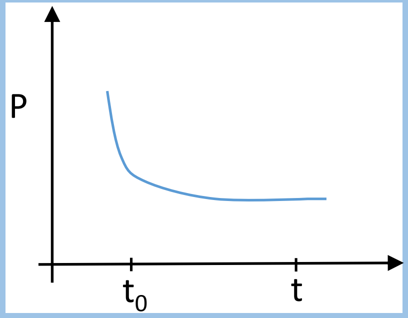
V_{sc} - volume of sample chamber
$\Delta p/\Delta t$ - pressure rise in the sample chamber measure by SRG
A - surface area of the sample chamber



- **Pump down curve (Throughput system 5.2)**

$$q_{out}(t) = p_{SC}(t) \times C_0$$

p_{SC} – SRG pressure
C_0- calculated conductance element



- **Outgassing rate**

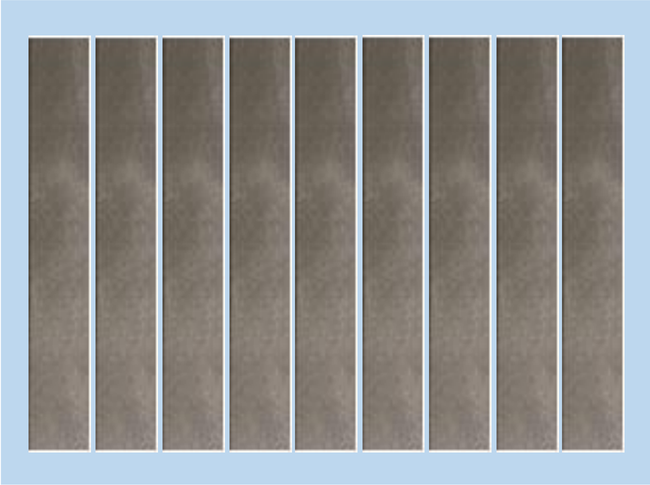
$$Q = \frac{q_{out}}{A} \ (Pa\ L\ s^{-1} cm^{-2})$$

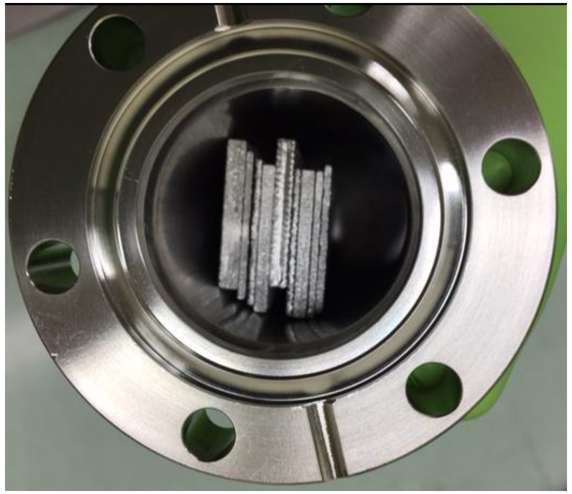
Q - Outgassing flow
A - Surface area of the sample

- Rate-of rise: H_2 Outgassing in baked system
- Pump-down curve: H_2O outgassing in unbaked system

Sample Materials (coupons):
3D-Printed Samples

3-D Printed Titanium Sheets (Ti 64)





- Surface area of the samples

  A = 496 cm^2

- Volume of the sheets

  V = 42.3 cm^3

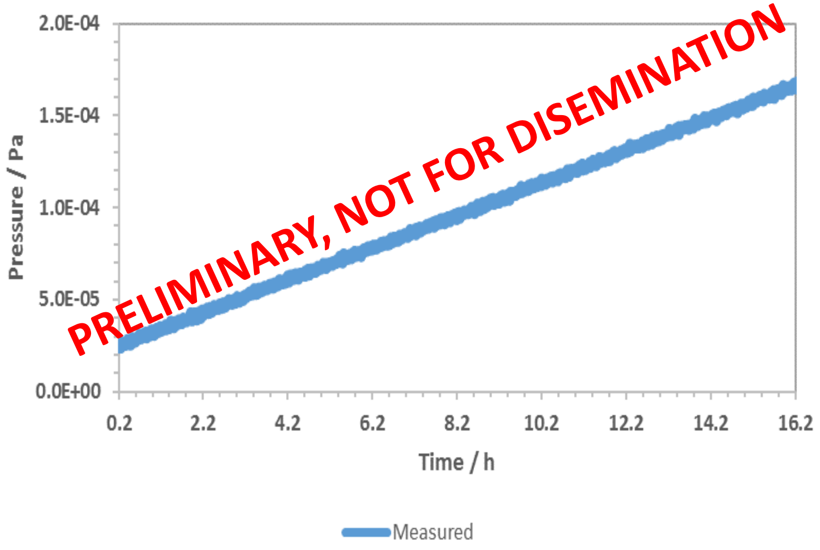
- Surface area of the samples chamber

  A = 212 cm^2

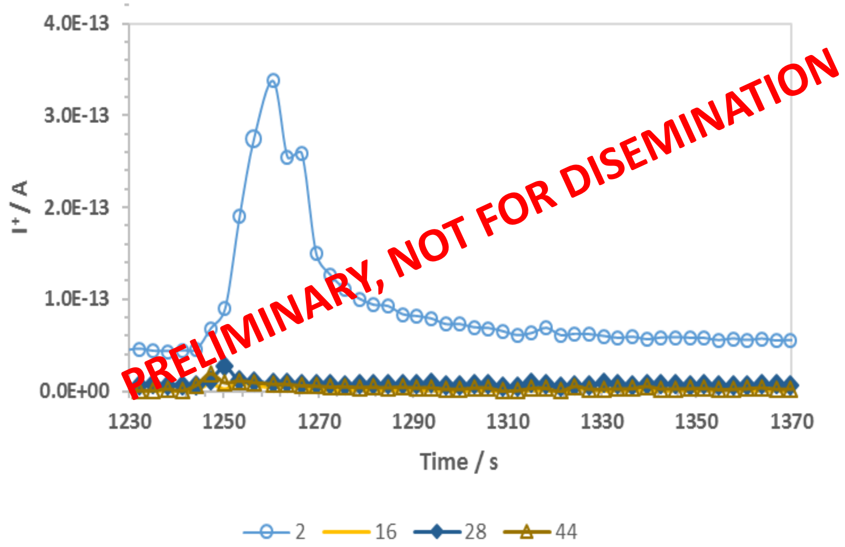
- Volume of the sheets

  V = 150 cm^3

Sample Materials (coupons):
3D-Printed Samples



Rate-of-rise data



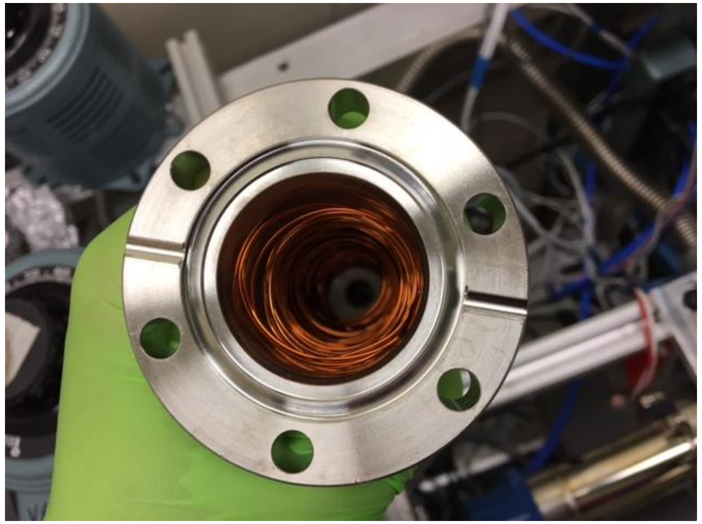
RGA signals of pressure burst

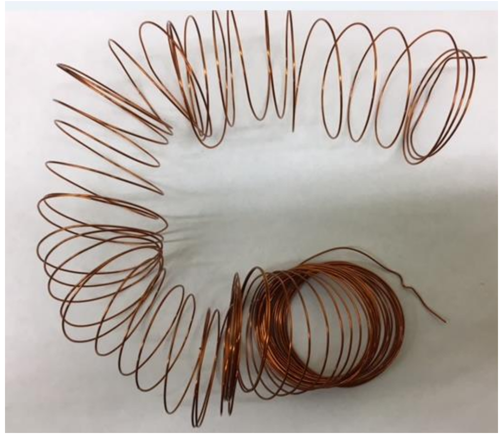
ISO document sufficiently covers measurement

Some issues to consider:

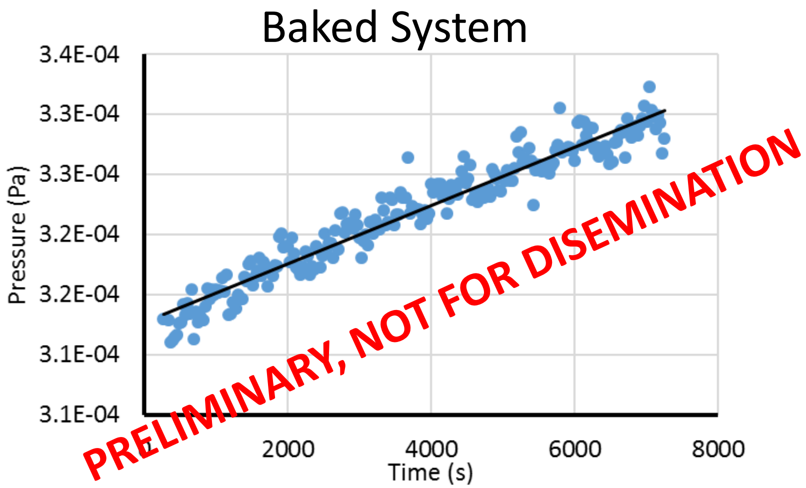
- Separation of samples
- Pumping or re-absorption by samples

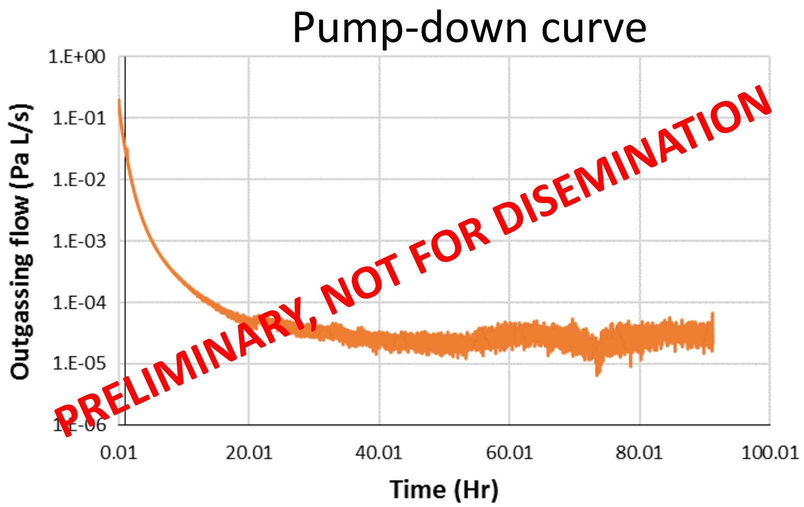
Sample Materials (coupons):
Practical components



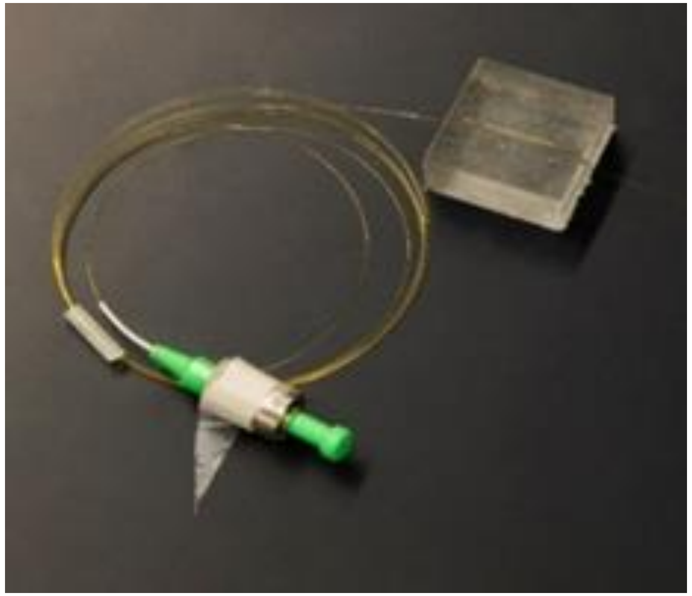


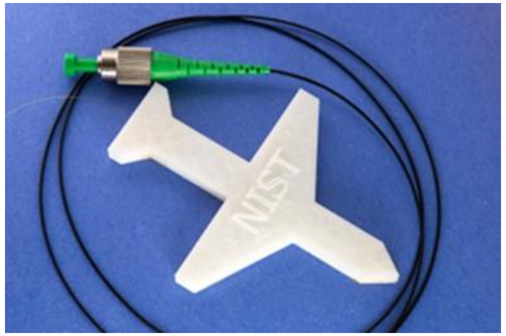
- ISO document sufficiently covers measurement for baked out components
- Pumpdown curves for unbaked samples not explicitly covered





Gas Absorption and Desorption





- Gas uptake and gas desorption of materials
- Embedded sensors
- Gas storage
- Sensors (selective gas uptake)

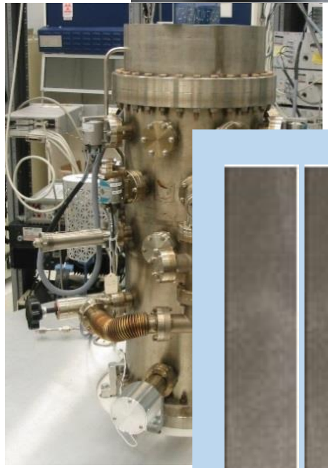
Example:
3D printed materials

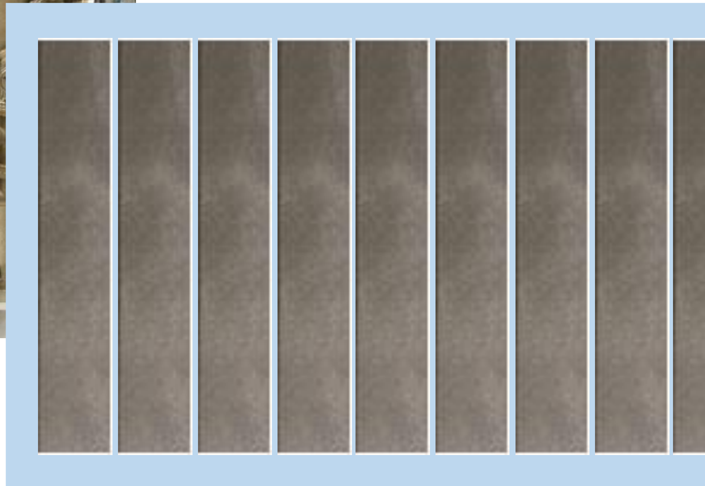
Test case: 3-D Printed Acrylonitrile Butadiene Styrene (ABS)

- Stores a lot of water
- High outgassing rate
- Fractional mass loss important

Outline

- Test Chambers and Components
- Real chambers
- Sample Materials (Coupons)
- **Comments on Working Draft ISO/PDTS 20177.5 Procedures to measure and report outgassing rates**





Comments: Problem with N_2 equivalent

3.4 nitrogen equivalent outgassing rate
outgassing rate when all gases released from the sample are assumed to be nitrogen molecules.

NOTE **To be consistent**, all quantities involved in a physical equation (e.g conductance and pumping speed) need to be expressed for nitrogen, if pressure is measured in nitrogen equivalent. Otherwise, the same nitrogen reading of a vacuum gauge could lead to different quantities dependent on gas species (see the following example).

This is only internally consistent in one lab, on one apparatus
Nitrogen equivalent language is then used throughout the document, especially in the procedures, and in section 8 for reporting.

6 Measurement procedures

The total outgassing rate may be determined in two ways:

1) The outgassing rate is determined for each detected gas species or for at least the major gas species separately and then all the determined outgassing rates are summed up to the total outgassing rate.

2) The total outgassing rate is directly determined as a **total outgassing rate in nitrogen equivalent**.

The **latter method is less accurate**, since the same true gas flow rate of a different gas species mixture may lead to a different nitrogen equivalent reading of the total pressure gauge.

NIST can agree with this last statement!

Comments: Why use N_2 equivalent?

- In the vast majority of cases outgassing will be dominated by:
  - H_2 in baked systems
  - H_2O in unbaked systems
- Why are some outgassing measurements reported in N_2 equivalent?
  - Gauges are typically calibrated with N_2
  - Some claim it facilities comparison with other measurements
    - **Not true:** Only if same type of gauge, same sensitivity to N_2
  - The problem is, the user of a reported N_2 outgassing rate must know
    1. The gauge that was used to measure it
    2. The sensitivity of the gauge
    3. What the true gas

Comments: Problem with N_2 equivalent

- N_2 equivalent is not SI-traceable
  - Gas-sensitive gauge is calibrated with N_2
  - Gas is H_2 (for example)
    - N_2 gauge sensitivity is SI-traceable only for N_2
    - Uncertainty on N_2 calibration factor is not correct for H_2

- If the gas composition is truly unknown, then any determination of the outgassing rate is meaningless if a gas-sensitive gauge is used.

- In the future, there will be alternative gauge technologies to SRGs, CDGs, and ion gauges.

Comments: Problem with N_2 equivalent

Example 1 : We have **1 X 10^{-11}** Pa L/s/cm^2 H_2 outgassing

N_2 equivalent if measured with SRG:	3.75 X 10^{-11}
N_2 equivalent if measured with Ion Gauge:	2.0 X 10^{-11}
N_2 Equivalent if measured with CDG:	1.0 X 10^{-11}

Manufacture reports N_2 eq. measured with SRG

User has ion gauge, sees a factor of 2 difference

User must have knowledge of manufactures measurement procedures and SRGs to accurately determine observed outgassing rate in their system

Comments: Problem with N_2 equivalent

Example 2 : We have **1 X 10^{-8}** Pa L/s H_2 outgassing

N_2 equivalent if measured with SRG:	3.75 X 10^{-8}
N_2 equivalent if measured with Ion Gauge:	2.0 X 10^{-8}
N_2 Equivalent if measured with CDG:	1.0 X 10^{-8}

Manufacture reports N_2 eq. measured with SRG

User has SRG, leaks in 1.0 X 10^{-6} Pa L/s of N_2

User believes outgassing is 4% of flow

Flow is actually 1% H_2.

User must have knowledge of manufactures measurement procedures and SRGs to accurately determine observed outgassing rate in their system

Comments: Alternative to N_2 equivalent language

6 Measurement procedures

The total outgassing rate may be determined in two ways:

1) The outgassing rate is determined for each detected gas species or for at least the major gas species separately and then all the determined outgassing rates are summed up to the total outgassing rate.

2) The gas composition has not been determined.

   a) For systems baked between 120 and 150 C for >48 hours, presume gas is H_2 and report H_2 outgassing rate

   b) For unbaked systems (less than 5 day since evacuation), presume gas is H_2O and report H_2O outgassing rate

The **latter method is less accurate**, since the same true gas flow rate of a different gas species mixture may lead to a different equivalent reading of the total pressure gauge. For new materials where the composition of the outgassing products are not known, the composition must be determined for an outgassing rate to be measured with a gas sensitive gauge.

Procedure for measuring H_2 or H_2O with N_2 calibrated gauge

1. Obtain N_2 equivalent reading
2. Convert using relative sensitivity factor r_x
3. Include u_{cal} and u_r in uncertainty budget

Examples

1. SRG: for H_2 use $r_x = 1$; $u_r = 3\%$ (k=2)
2. CDG; No conversion necessary

Summary

- **Total Outgassing Gas Rate: $Pa \cdot L \cdot s^{-1} \cdot cm^{-2}$ should be added to section 4.**
  - **Recommend use**
- Consider revising "23±7 °C, should not change by more than 2 °C during measurement" (6)
- Consider adding pumpdown curve, 2-parameter power law fit
- Consider section on sample types and background subtraction for each type of sample
- Revise nitrogen equivalent language

Thank You!