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CAPE TOWN • SOUTH AFRICA • 21 - 26 JULY

Tips and Tricks of the trade: Building instrumentation for Atmospheric Mercury

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 - University of Colorado Boulder: Rainer Volkamer
 - University of Utah: Gannet Hallar



(Tyler Elgiar is now with the U.S. Bureau of Land Management)

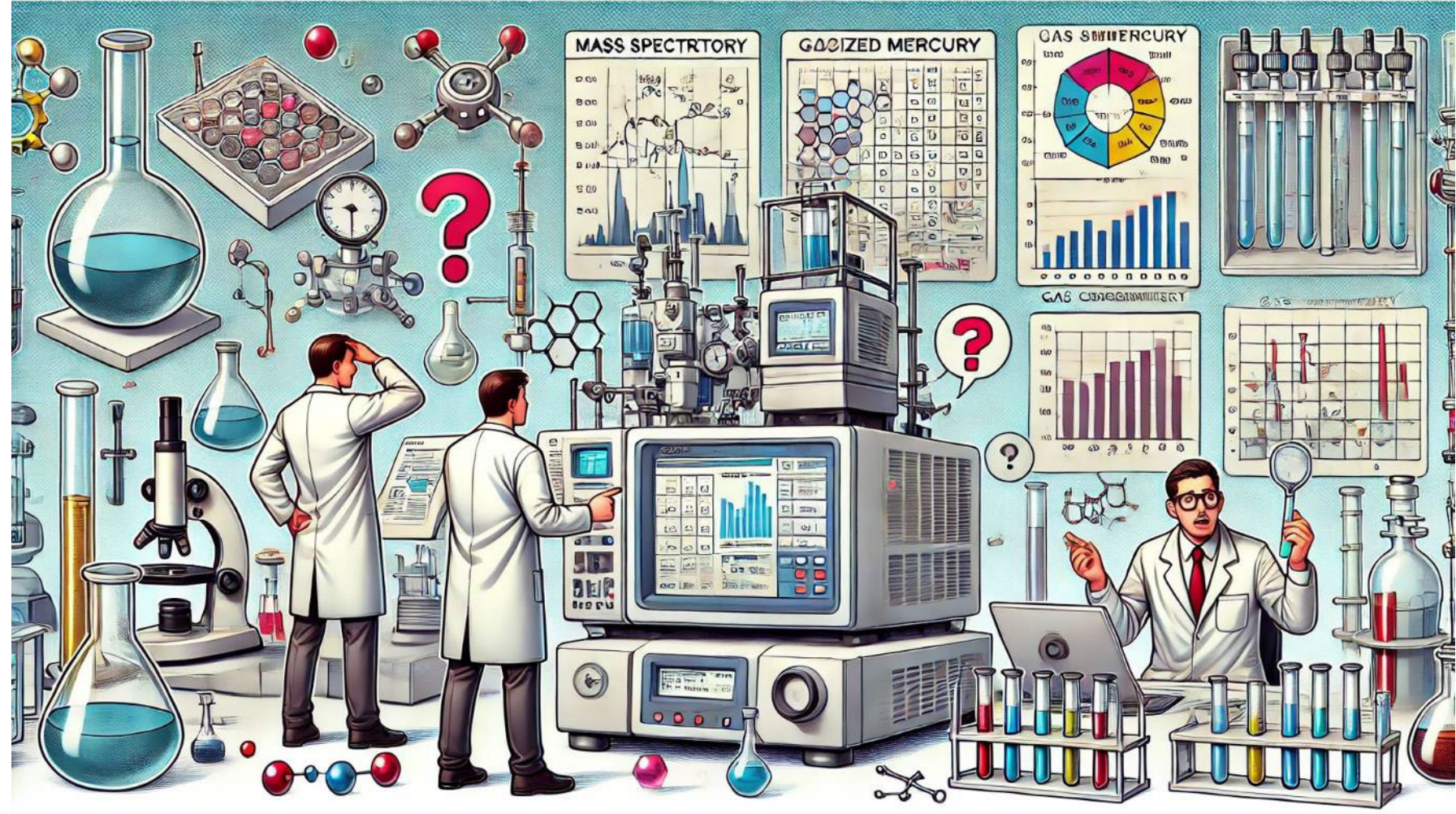
Oxidized Mercury is a Special Analytical Challenge



extremely labile

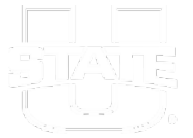
Interferences

- ozone
- H₂O
- particulate bound
- etc....



Hg^{II} sticks to EVERYTHING!

what are we measuring?



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Utah State University



Storm Peak Observatory, Colorado USA

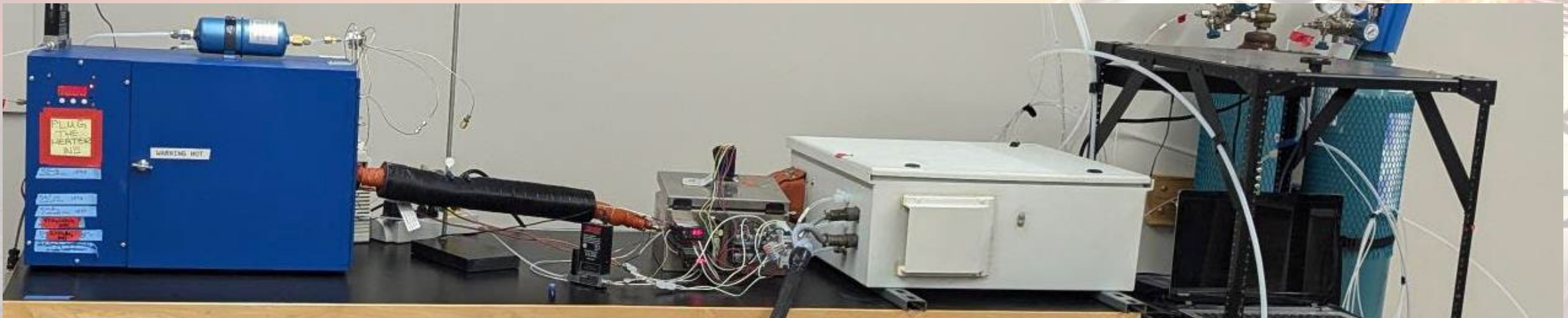
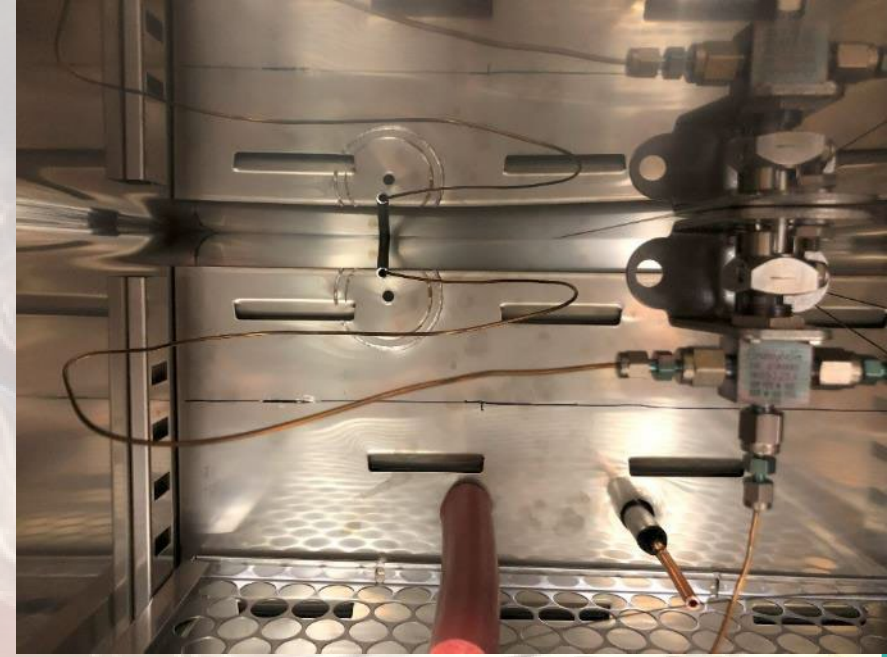
Elgiar
Thesis DOI



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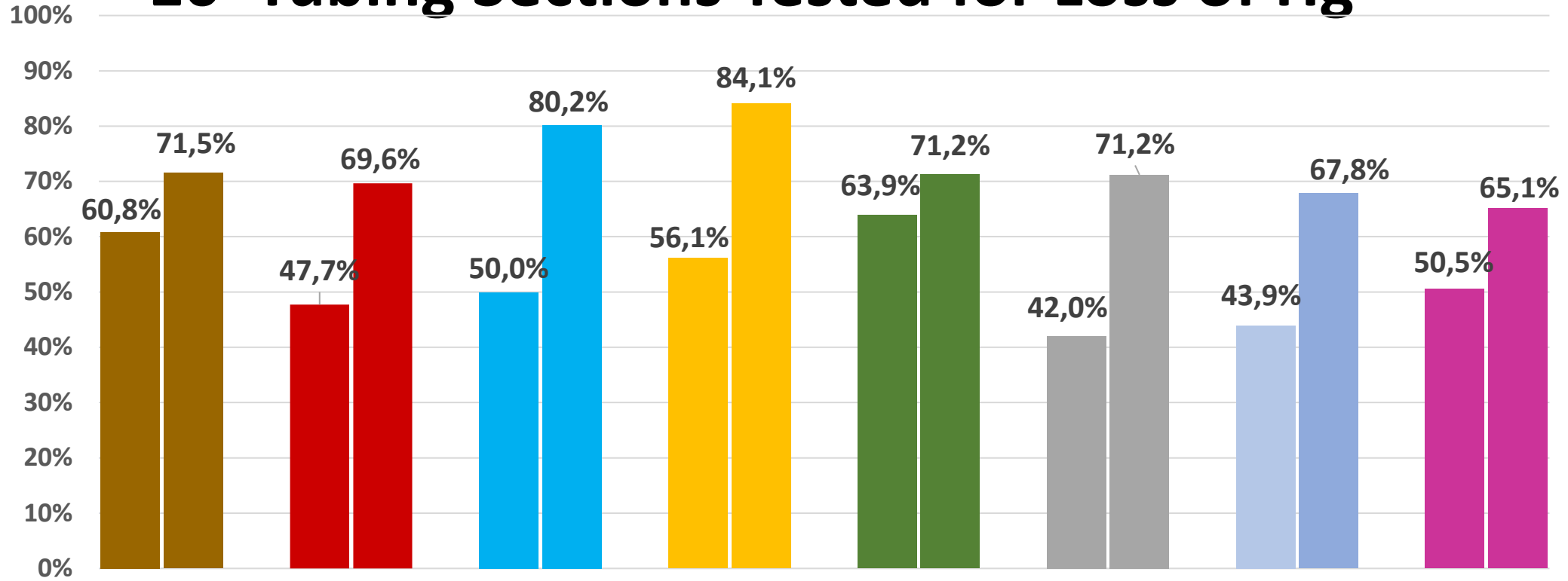
Transfer pathway

- Shortest path length possible!
- Hot temperatures. 120-180C
- Plan on long-ish equilibration times
- Alternative materials needs investigated further?
- Minimal dead space throughout flow path
- Conversion of oxidized to elemental Hg.



10' Tubing Sections Tested for Loss of Hg^{II}

% Hg^{II} observed



Perm tube temp 50°C 70°C 50°C 70°C 50°C 70°C 50°C 70°C 50°C 70°C 50°C 70°C 50°C 70°C 50°C 70°C

Control Sulfonert

Sulfonert

PEEK

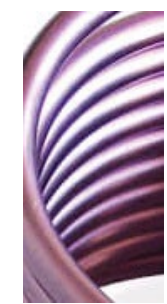
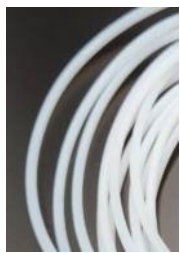
PFA

Silcosteel

PTFE

Durasan

Silonite

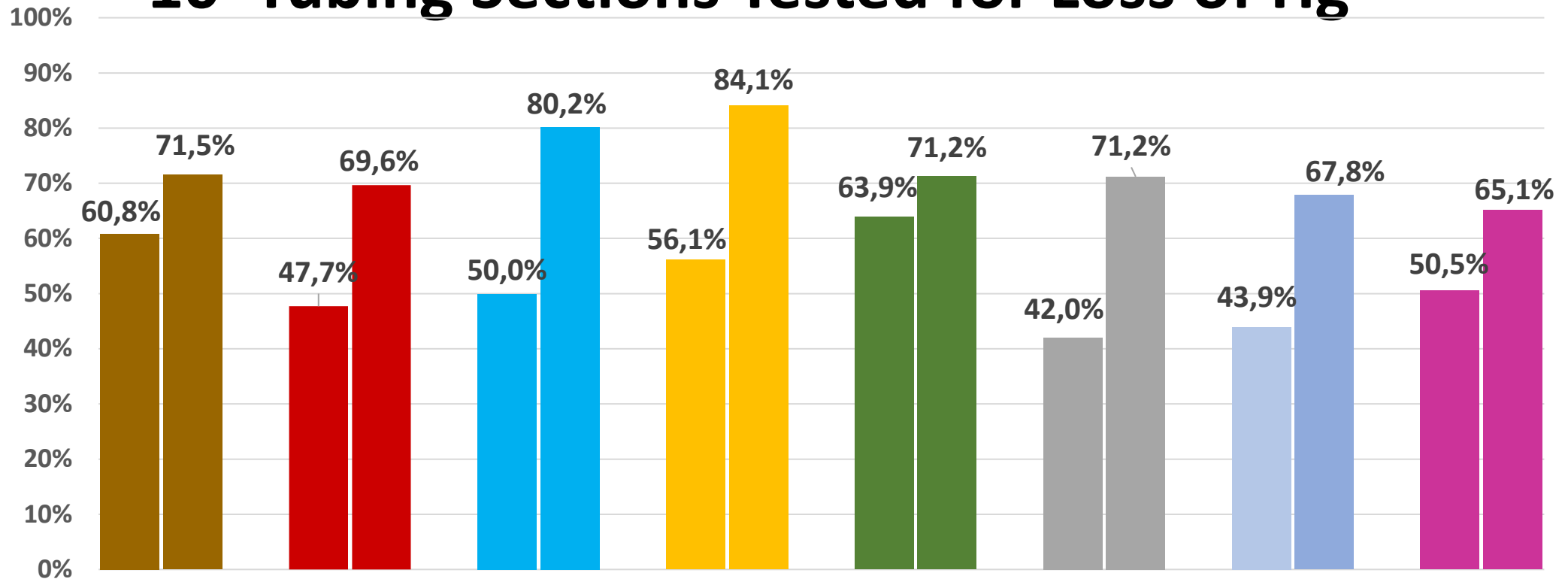


Being Used

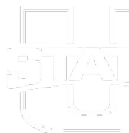
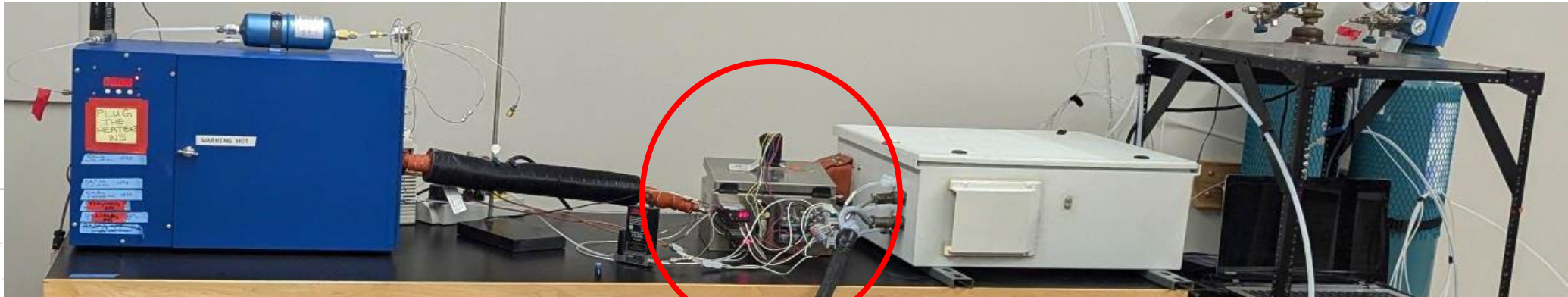


10' Tubing Sections Tested for Loss of Hg^{II}

% Hg^{II} observed

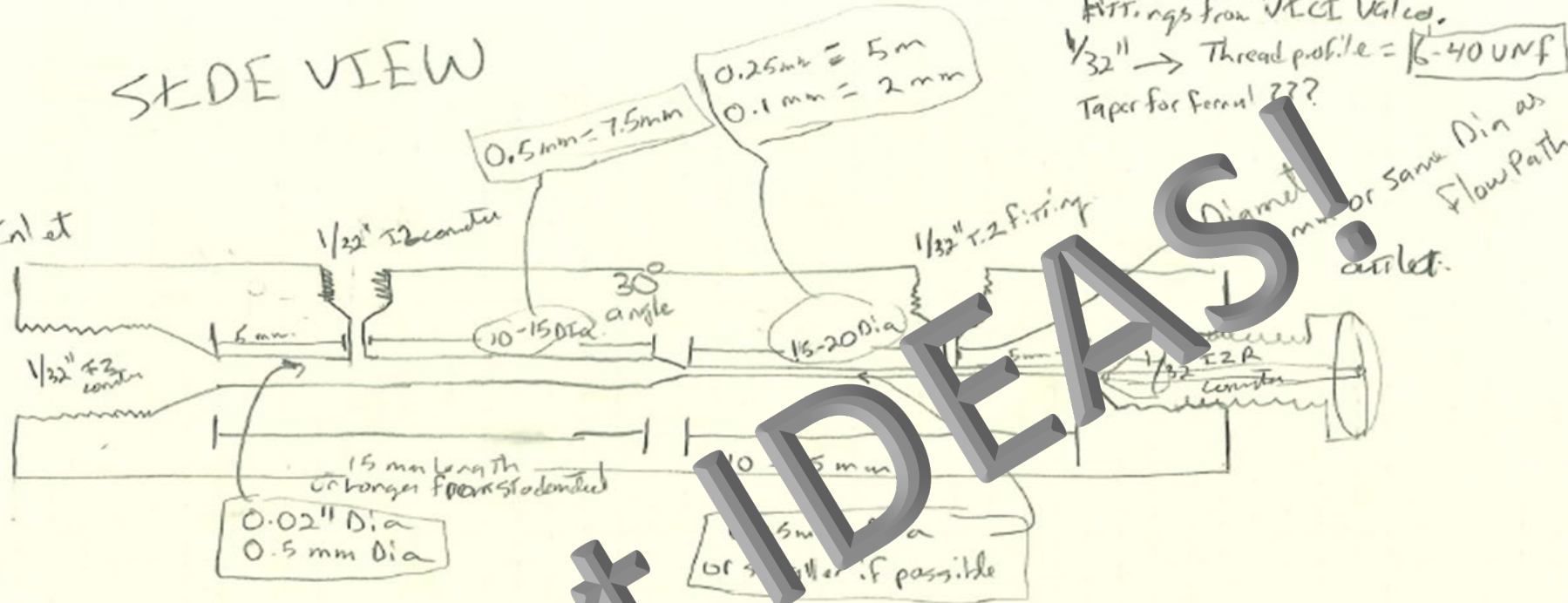


Perm tube temp 50°C 70°C 50°C 70°C 50°C 70°C 50°C 70°C 50°C 70°C 50°C 70°C 50°C 70°C 50°C 70°C



SIDE VIEW

Inlet

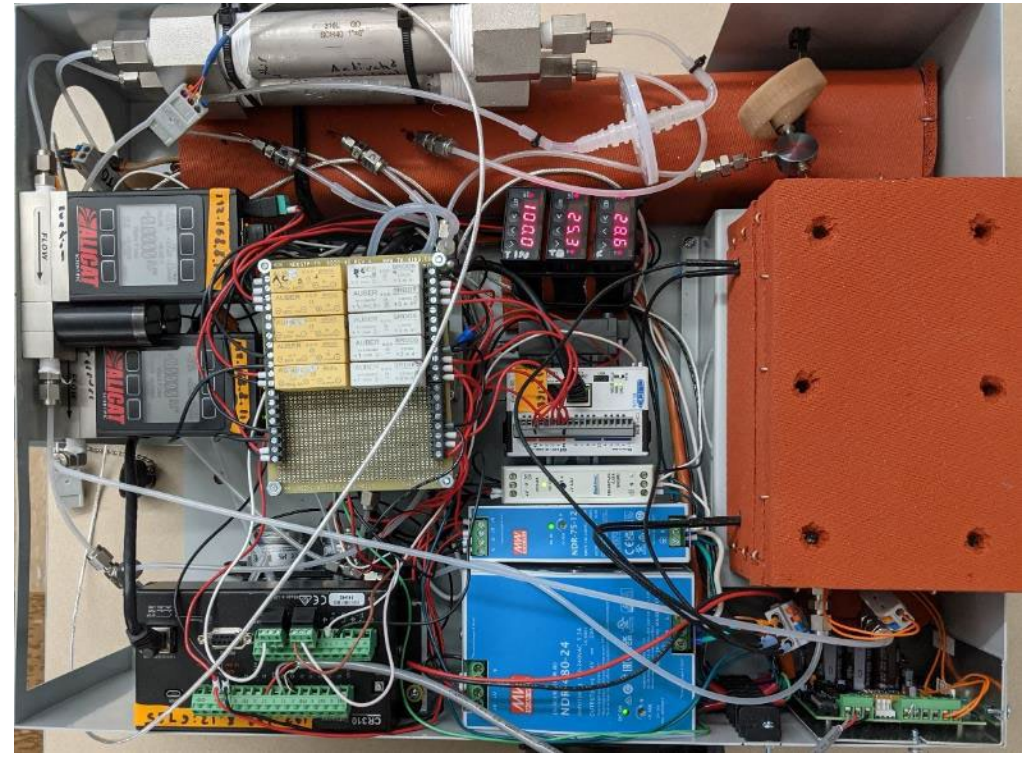
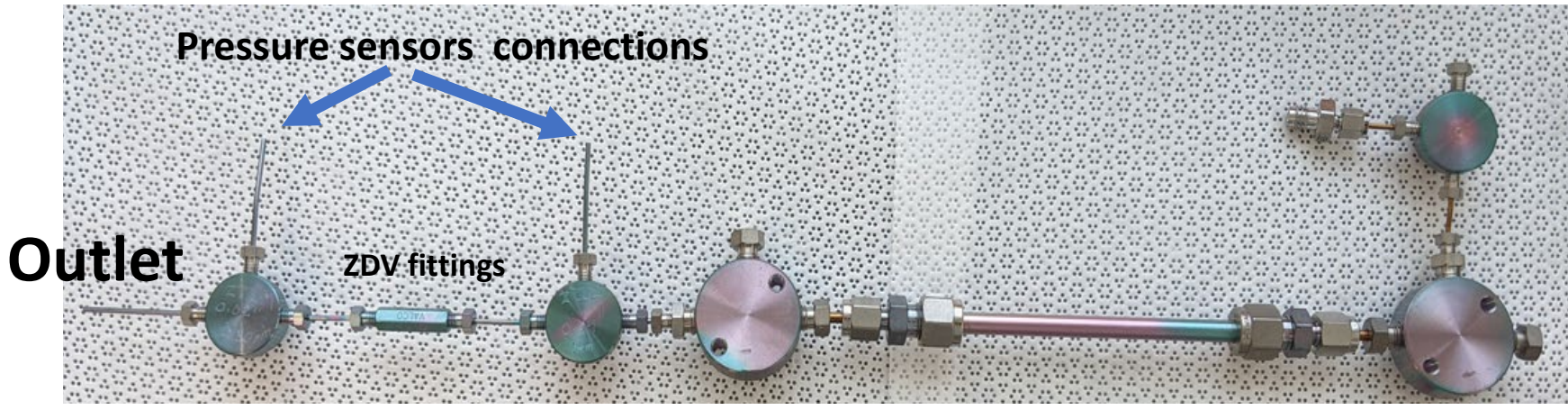


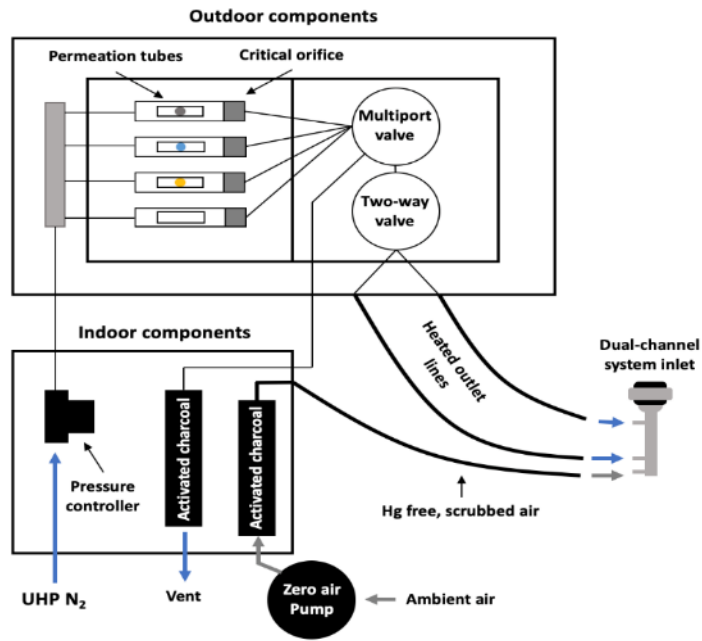
Fittings from VCCI Valves.
 $1/32'' \rightarrow$ Thread profile = $6-40 \text{ UMF}$
 Taper for ferrul ???

Concept IDEAS!

Material Aluminum or SS Depending.
 & Extend shape Not critical. (Round Disk - like valves of 3 way Tees works.
 or Square

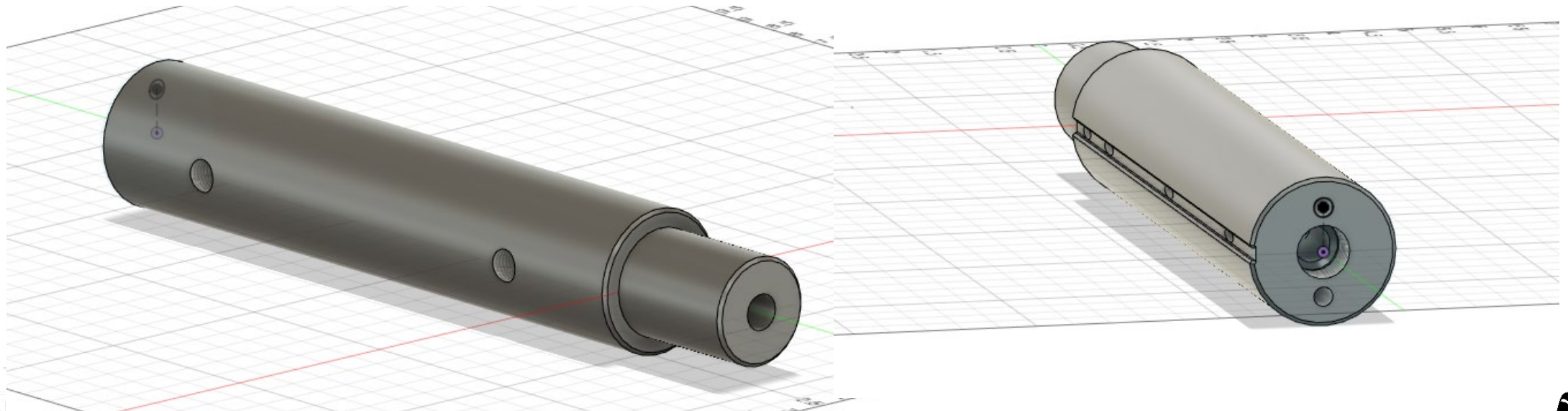
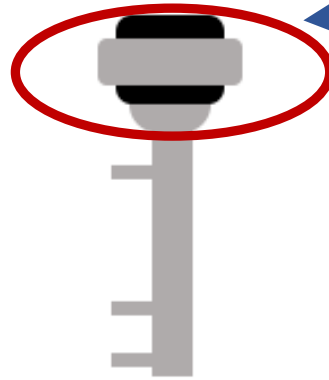






Dual-channel system inlet

Impactor housing

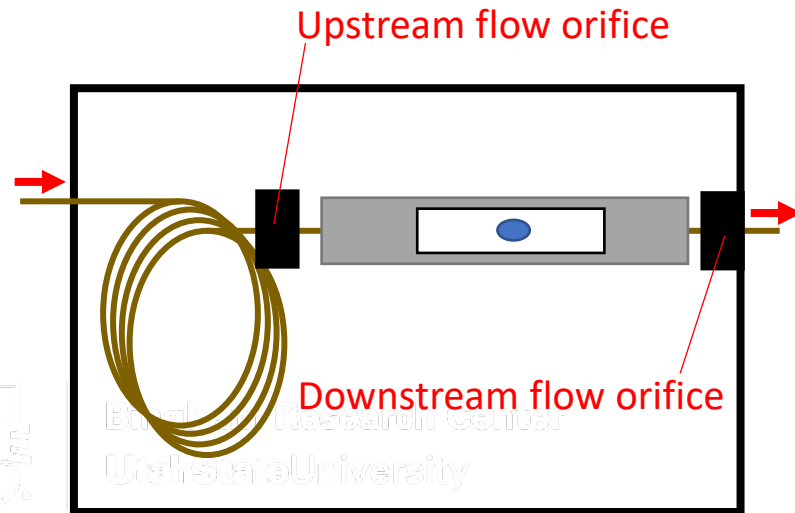
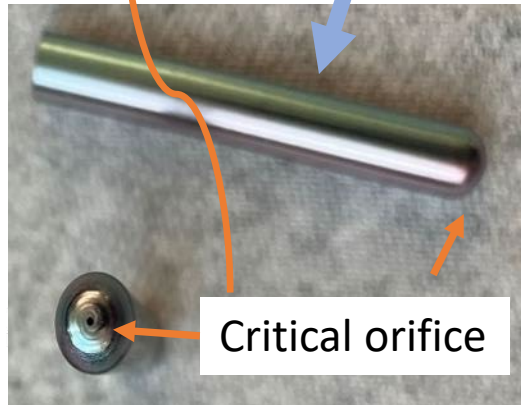
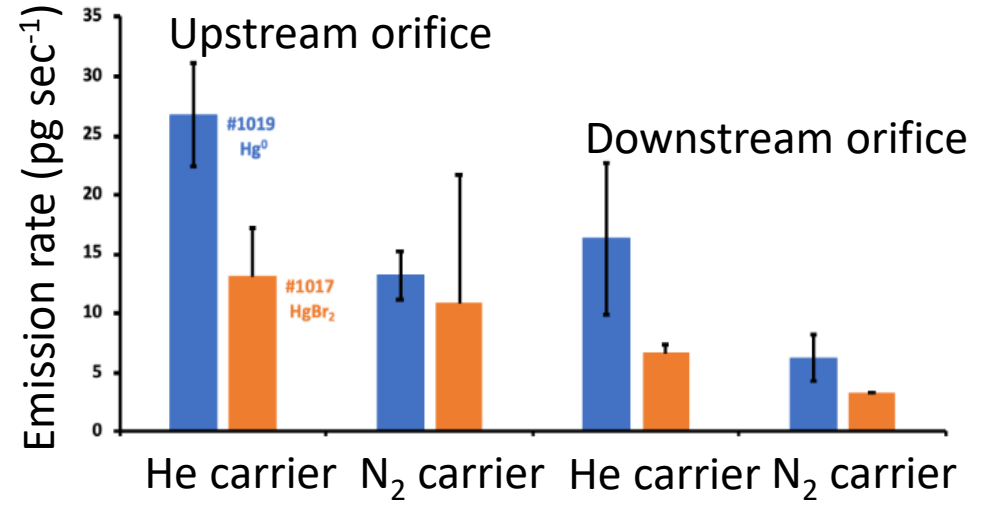
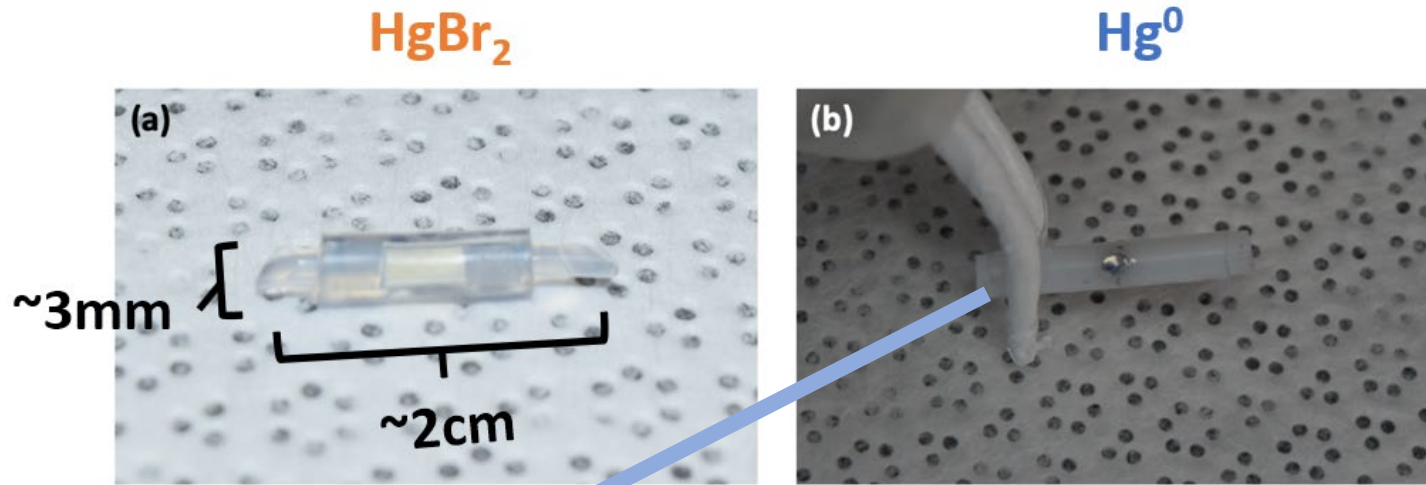


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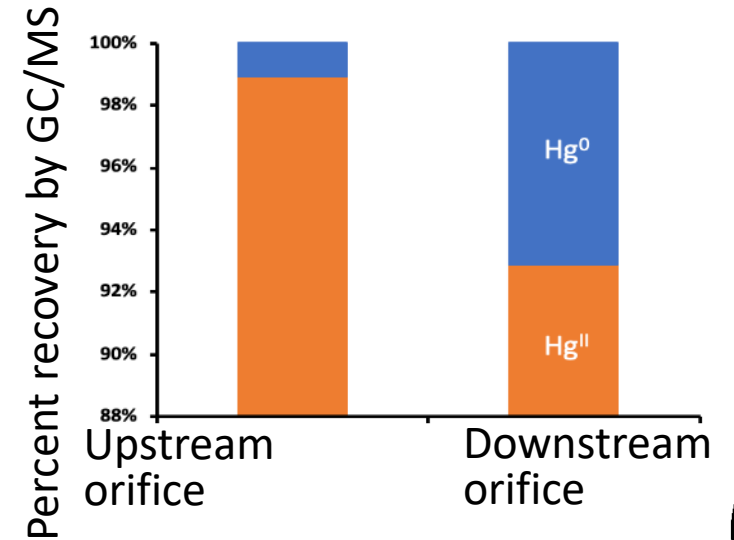


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Little things matter: Carrier gas & Flow orifice placement



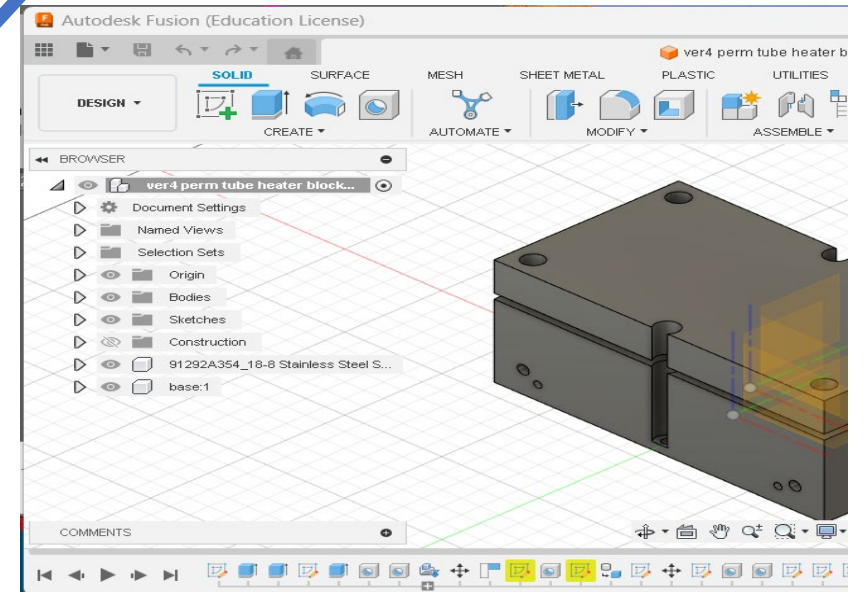
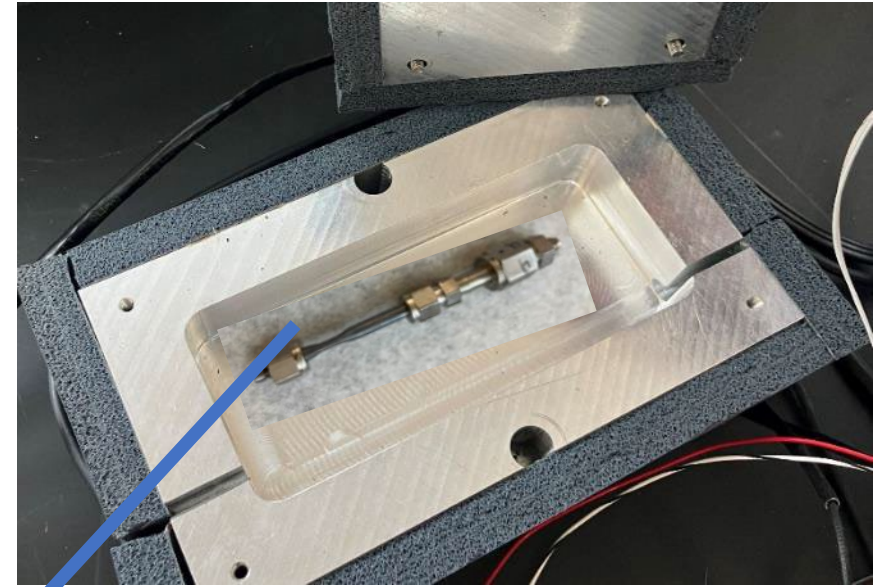
Elgiar et al. 2024



Calibrator 1



Perm Tube Stability



Calibrator 2



Calibrator 3



Jones et al., 2016

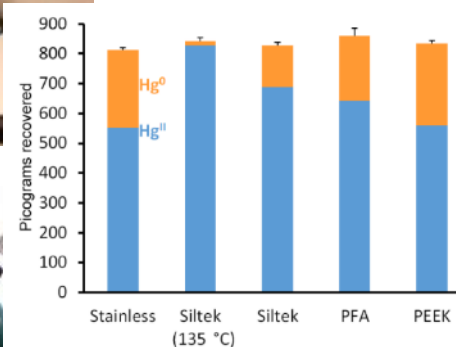
GCMS work



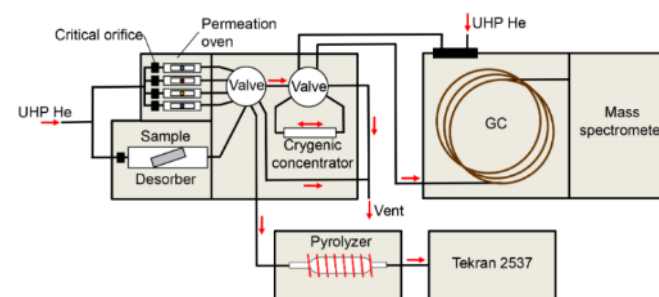
Successes!

able to separate and identify Hg halides low enough for ambient air collections (90pg).

Able to coordinate all the parts to produce data!!!!



Needs some more work
HgO and Hg(NO)₃ where are you?
Better interface for the user.



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Where we've come since then

Built a much more beautiful GC-MS system for UNR

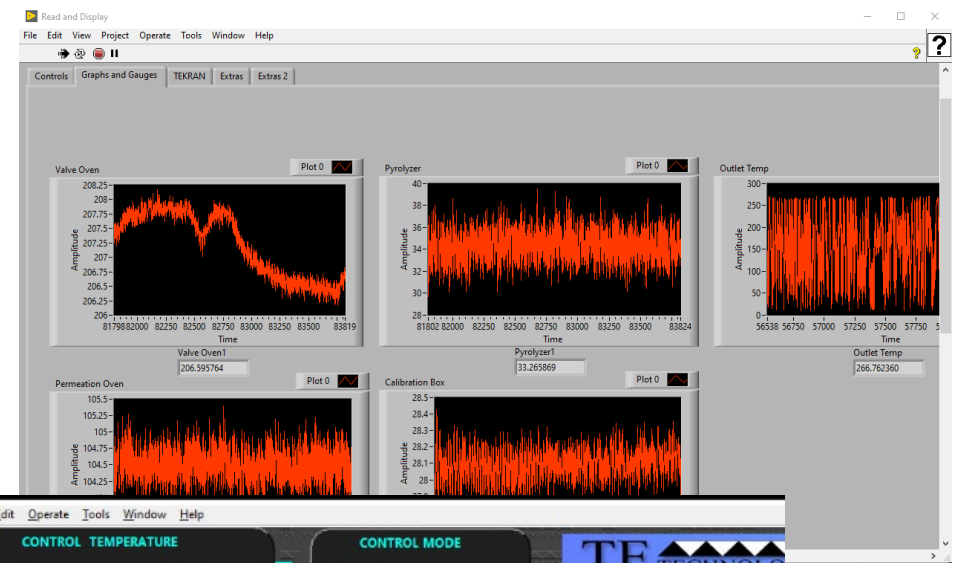
New materials and designs we tried created a lot of problems



```

131 Public permsettimer
132 'perm oven safety shutoff
133 Public permshutofftimer
134
135 'variables for click PLC Plus unit. C2-01CPU
136 Public Click_PLC_ModbusResult 'brings back to the campbell the variables from
137 'fan_chassis unit
138 Public Setpoint_chassistem = 30 'Temperature setpoint for the FAN ClickPLC =
139 Public TEMP_chassis_fan 'Temperature of fan ClickPLC =DF12 = modbus 428695(
140 'Public NEW_Setpoint_chassis' write new temperature set point into the ClickPI
141 Public RTD_fail_Chassis_fan 'this is to set the tempt to zero if there is a bu
142 'Temp out heater
143 Public Current_Setpoint_T_O 'Temperature setpoint for the outline ClickPLC =
144 Public TEMP_T_O 'Temperature of outline ClickPLC =DF37 = modbus 428745(raw)(
145 Public NEW_Setpoint_T_O = 150 'write new temperature set point into the Clicki
146 Public RTD_fail_T_O' this is to set the tempt to zero if there is a burnout of
147 'Temp inside heater
148 Public Current_Setpoint_T_IN 'Temperature setpoint for the insideline Clicki
149 Public TEMP_T_IN 'Temperature setpoint for insideline ClickPLC =DF62 = modbu
150 Public NEW_Setpoint_T_IN = 150 ' write new temperature set point into Click PI
151 Public RTD_fail_T_IN 'this is to set the tempt to zero if there is a burnout
152 'error
153 Public Click_PLC_error
154 'Public Autotune_PID
155 Public Autotune_PID
156 Public Autotune_PID
157 Public Fan '=1
158 Public sucypump = 1
159 Public prespump = 1
160 Public Permtube_valve
161 'Click PLC UNITS
162 'Units Current_Setpoi
163 Units TEMP_chassis_fa
164 Units Current_Setpoir
165 Units TEMP_T_O= deg C
166 Units Current_Setpoir
167 Units TEMP_T_IN = deg
168
169 'killheaters is the s
170 Public killheaters
171 Public heatertemps As
172
173 'calibration timing s
174 Public calibrating
175 Public calib_durat

```



The screenshot displays the CLICK Programming Software interface. The main window shows a ladder logic program with three rungs. The first rung contains a 'Copy' instruction with source 'input_temp_chassis' (address DF76) and destination 'input_temp_chassis' (address DF12). The second rung contains a 'Copy' instruction with source 'input_temp_outline' (address DF77) and destination 'T_O_PV_ProcessRaw' (address DF37). The third rung contains a 'Copy' instruction with source 'input_temp_in line' (address DF78) and destination 'T_IN_PV_ProcessRaw' (address DF37). The interface includes a menu bar, a toolbar, a project tree on the left, and a status bar at the bottom.

The screenshot shows a control interface for a TE TECHNOLOGIES system. The main display area is divided into several sections:

- CONTROL TEMPERATURE:** Features a 'SELECT' button, a 'SET TEMPERATURE' of 10.00 °C, and a 'TEMPERATURE SENSOR' reading of 24.73 °C.
- CONTROL MODE:** Includes a 'SELECT' button.
- CONTROLLER ADDRESS:** Shows the address '99'.
- OUTPUT:** Includes a 'SELECT' button and an 'ON' button.
- CONTROLLER OPTIONS:** Includes a 'SELECT' button.
- ALARMS:** Includes a 'SELECT' button.
- SEARCH 1 TO:** Shows '99' and a 'SEARCHING' progress bar.
- ON / OFF:** A large green 'ON' button is visible.
- TEMPERATURE:** A vertical scale from -30 to 30 is shown on the right side.



What we wanted

- NIST tracibility,
- Field deployable
- Integrated data collection

what we got!

- NIST tracibility, YES!!!
- Field deployable
 - yes but we can do better!!!
- Integrated data collection
 - We have this and it can be improved



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Summary.

- **All surfaces retain some oxidized mercury and result in some reduction to elemental form.**
- **Delivery systems need equilibration times of hour(s) due wall surface interaction**
- **Permeation tube based oxidized Hg needs hot temperatures to prevent sticking to surfaces in flow path. 120°-180°C. Without thermally converting to elemental Hg**
- **Shortest flow path with high passthrough rates and appropriate carrier gas**
- **Integrated instrument analytics. Proper instrument parameters tracking**
- **Keeping systems similar for proper comparability sometimes small differences =large changes in outcome.**



QUESTIONS?



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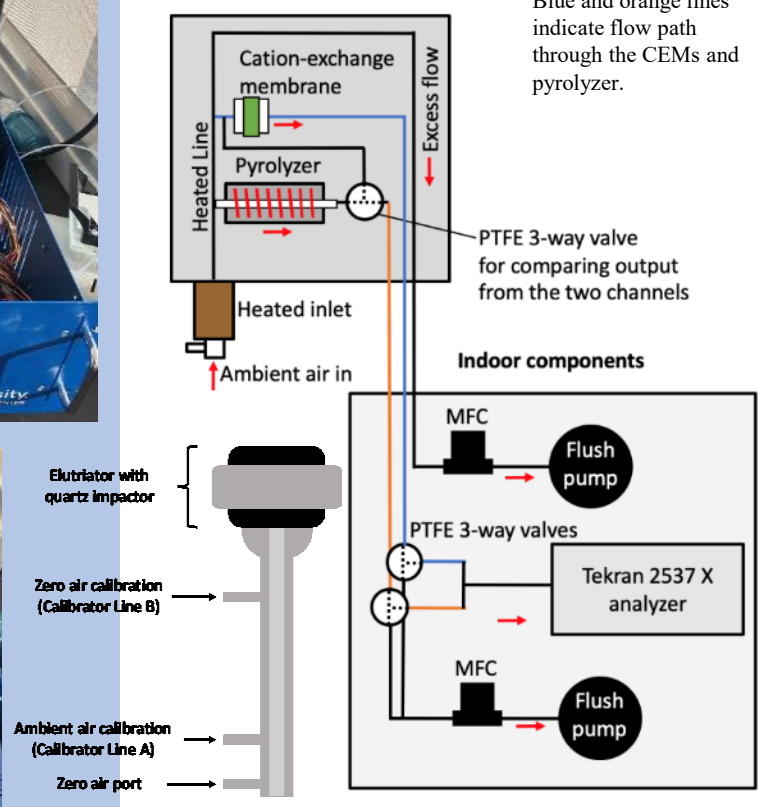


USU dual channel mercury analysis system



Control box CR1000x datalogger, power supplies, switching valves, communications, and flow controllers.

system

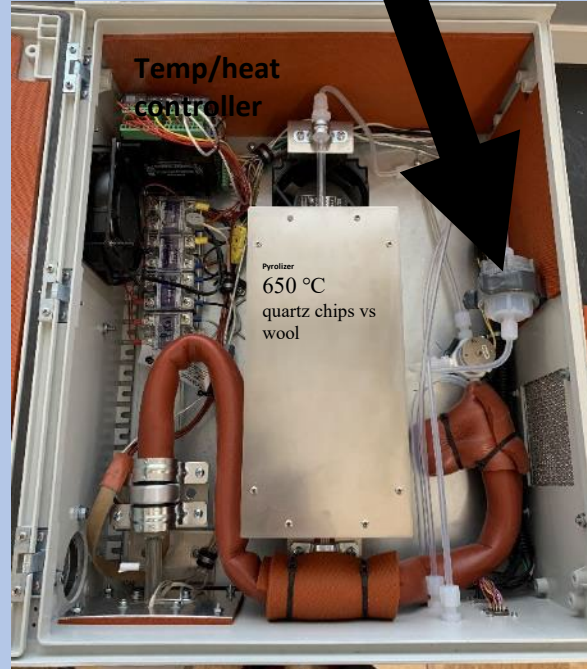


Blue and orange lines indicate flow path through the CEMs and pyrolyzer.



two cation-exchange membranes (CEMs) collect Hg^{II} and allowed Hg^0 to pass through producing an Hg^0 measurement

Cation-exchange membrane



Temp/heat controller

Pyrolyzer
650 °C
quartz chips vs wool

Ambient Hg^0 and Hg^{II} were measured while deployed for 2 years at Storm peak laboratory in the Rocky Mountains ~3200 M a.s.l.

- NIST-Traceable calibration standards with recovery $\pm 10\%$
- Detection limit for Hg^{II} of $11.8 \pm 6.5 \text{ pg m}^{-3}$ and $5.8 \pm 1.9 \text{ pg m}^{-3}$ for the two sampling periods at Storm Peak. Detection limits calculated as 3 times the standard deviation of Hg^{II} concentrations. A PTFE valve was used to route pyrolyzed sample into the CEMs channel for determining bias between the channels, and for detection limit calculations.
- Flow directed at 1 L min^{-1} into one of two channels.
- First, utilizing pyrolyzer heated to $650 \text{ }^\circ\text{C}$, converting all Hg into Hg^0 .
- Second, two cation-exchange membranes (CEMs) which collect Hg^{II} and allowed Hg^0 to pass through producing Hg^0 without Hg^{II} .
- Hg^{II} was calculated by taking the difference between the two channels (total $Hg - Hg^0 = Hg^{II}$)
- Tekran 2537X Hg^0 analyzer sequentially received each sampling channel in 5 minute increments. Flow from unused channel is measured through a mass flow controller.

Heated inlet, total flow of 9 L min^{-1} using a quartz impactor at $2.5 \text{ }\mu\text{m}$ cut point with custom designed ports for calibration purposes.

