ICMGP 2024

CAPE TOWN • SOUTH AFRICA • 21 - 26 JULY

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Advancing Permeation Tube-based Mercury Calibration

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Acknowledgements

- Funding provided by the U.S. National Science Foundation
- This work involves and owes much to:
  - Utah State University: Trevor O'Neil, KarLee Zager
  - Reed College: Lynne Gratz, Ellie Derry
  - University of Nevada, Reno: Mae Gustin, Sarrah Dunham-Cheatham, Jan Gacnik (now at Jožef Stefan Institute), Livia Lown
  - Jožef Stefan Institute: Milena Horvat, Igor Zivkovic, Sreekanth Vijayakumaran Nair, Teodor Andron
  - University of Colorado Boulder: Rainer Volkamer
  - University of Utah: Gannet Hallar

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

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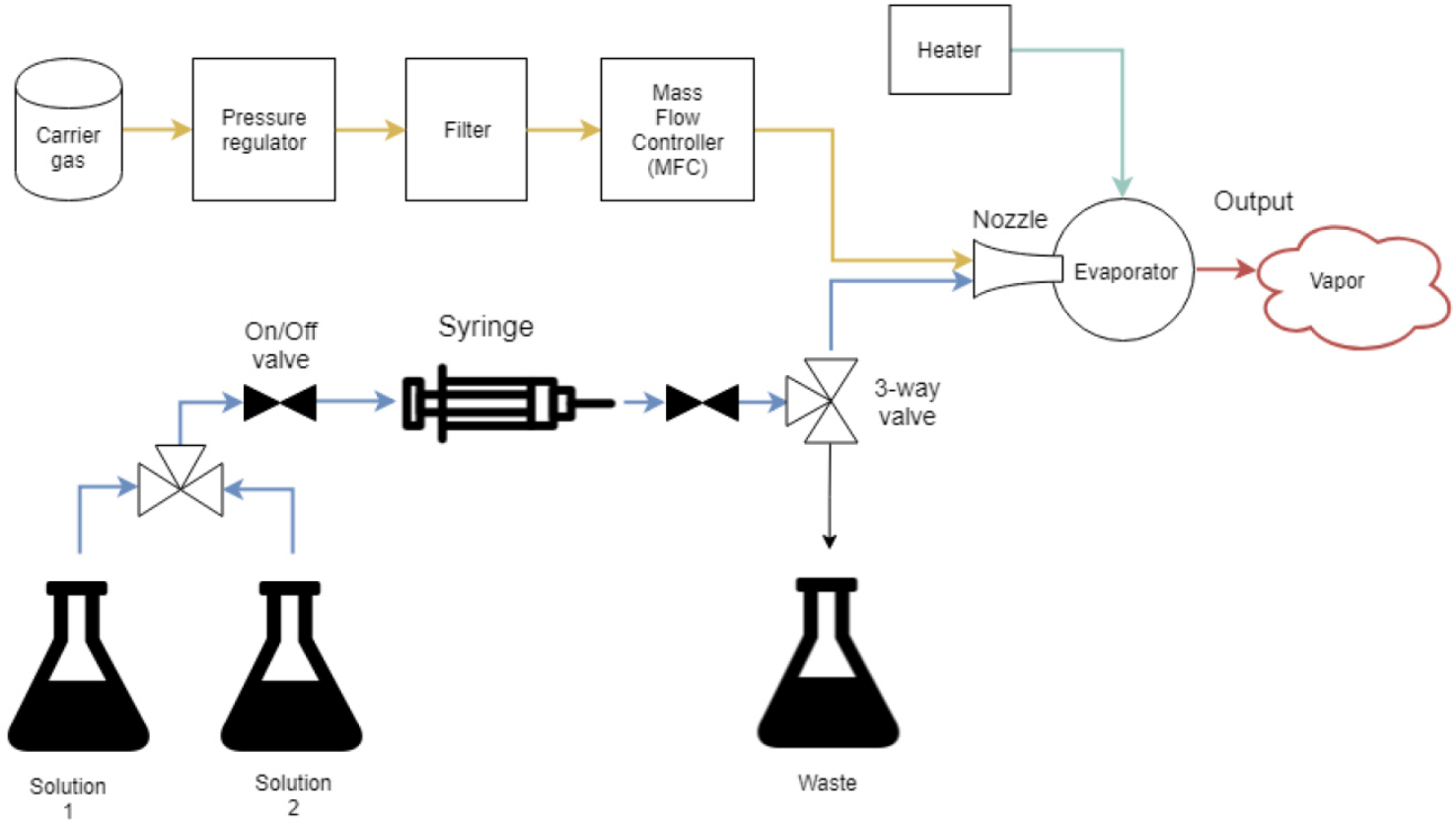
B. It took a decade and more to figure this out because no field-deployable calibration system existed

C. We need methods for SI-traceable Hg^{II} calibration so we don't repeat past mistakes

Options for SI-traceable calibration

Options for SI-traceable calibration

1. Aspiration or evaporation of liquid standards



Sari et al., 2019, Gacnik et al., 2021

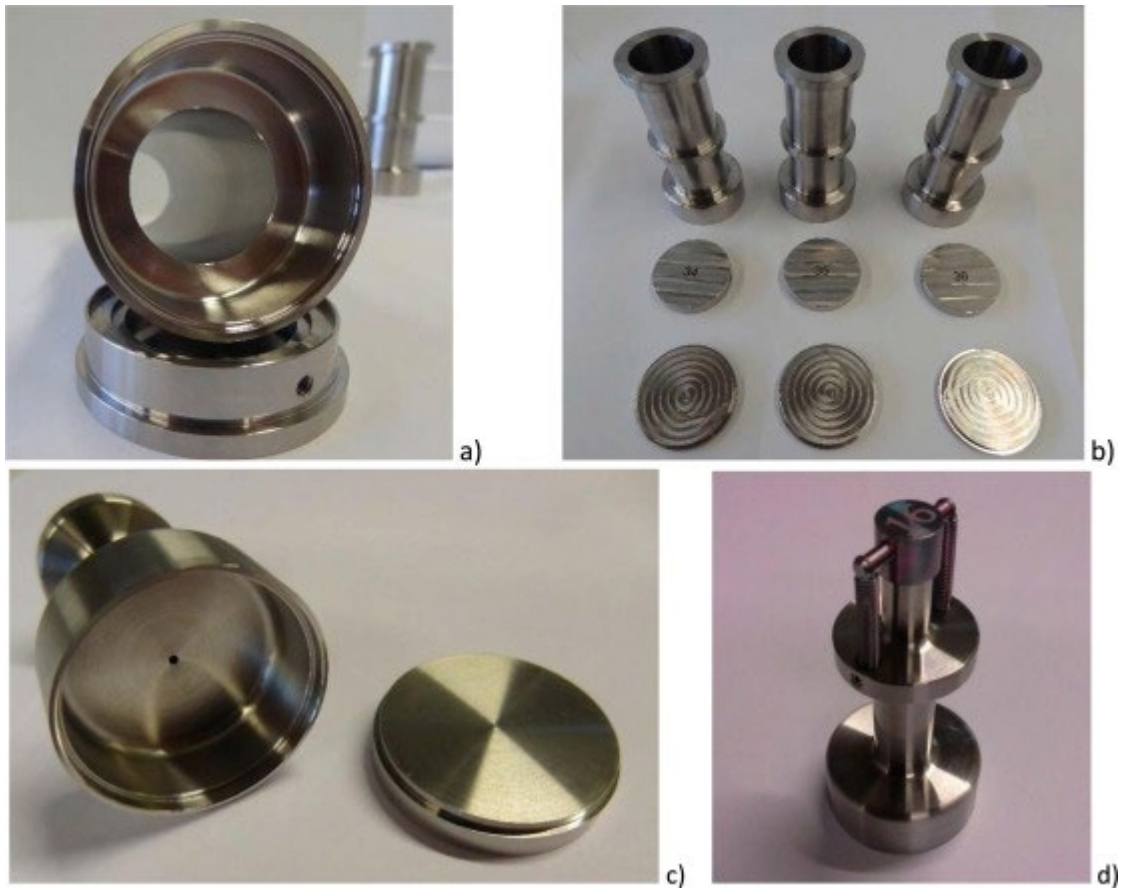
Options for SI-traceable calibration

2. Flow over a saturated bed

PS Analytical Mercury Vapour Generator

Options for SI-traceable calibration

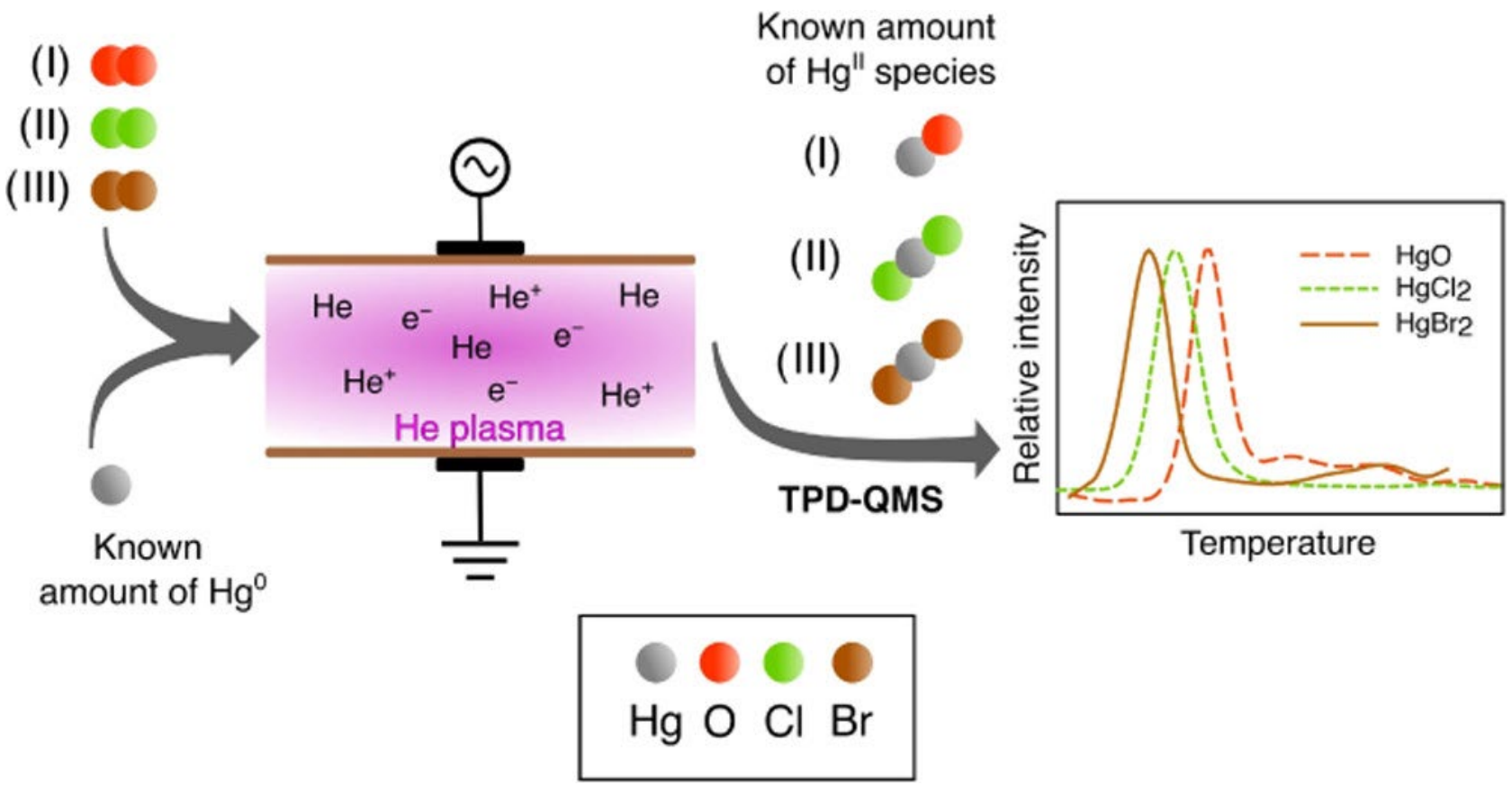
3. Diffusion tubes



Xiao et al., 1997; Swartzendruber et al., 2009; de Krom et al. (multiple; for Hg^0)

Options for SI-traceable calibration

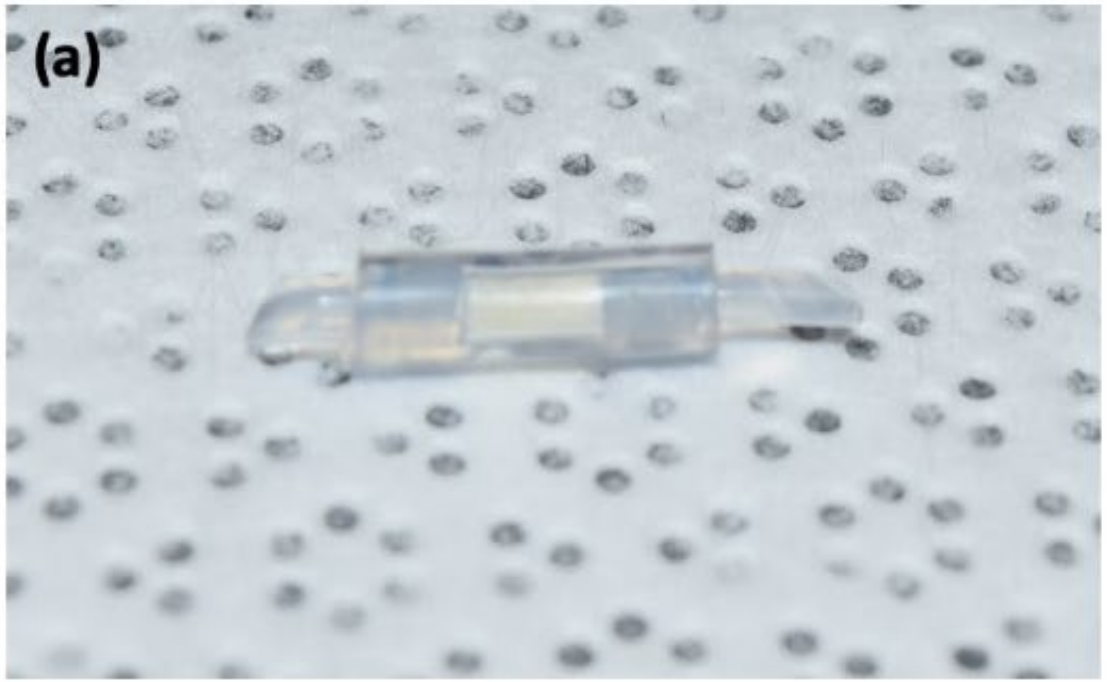
4. Direct Hg^0 oxidation

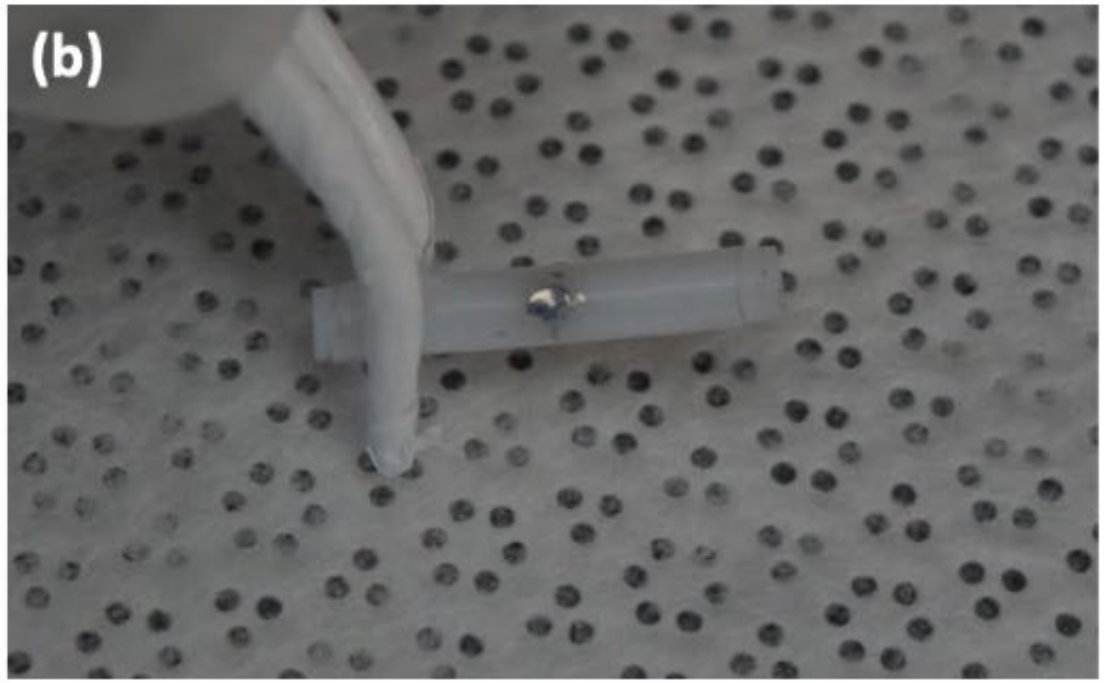


Gacnik et al., 2022

Options for SI-traceable calibration

5. Permeation tubes





First used by Landis et al., 2002?

Why are we putting our effort into permeation tube methods?

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- Capable of low, continuous emission rates
- Shown to work in real field conditions
- Confidence in identification of compound emitted
- Simple (in principle)

Basic principles of our method

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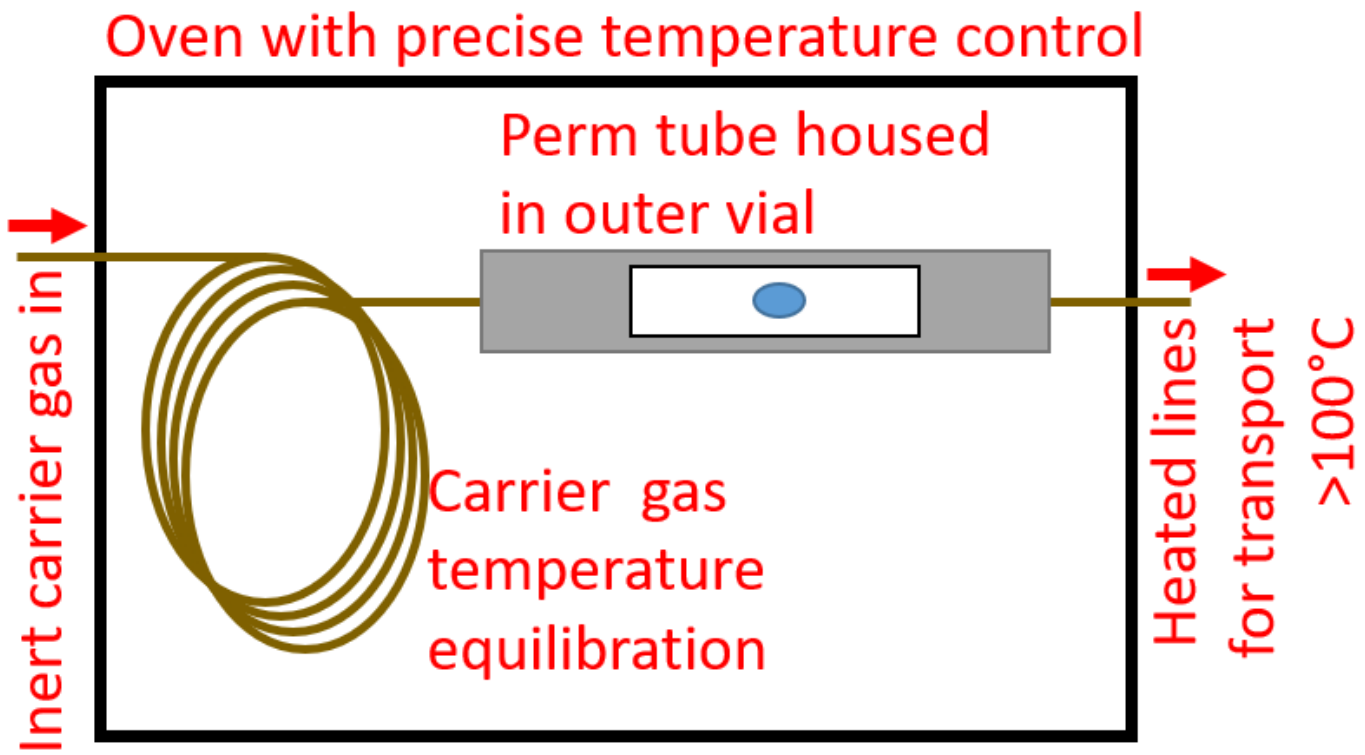
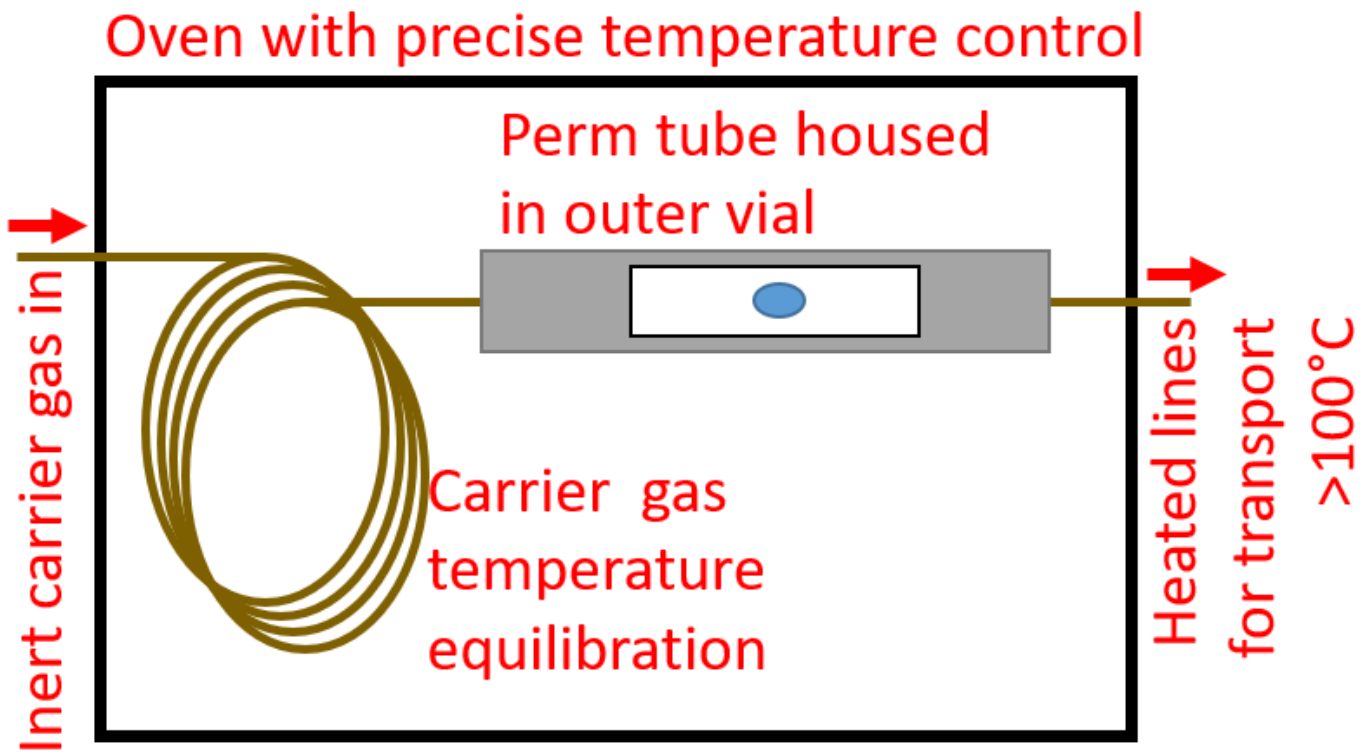
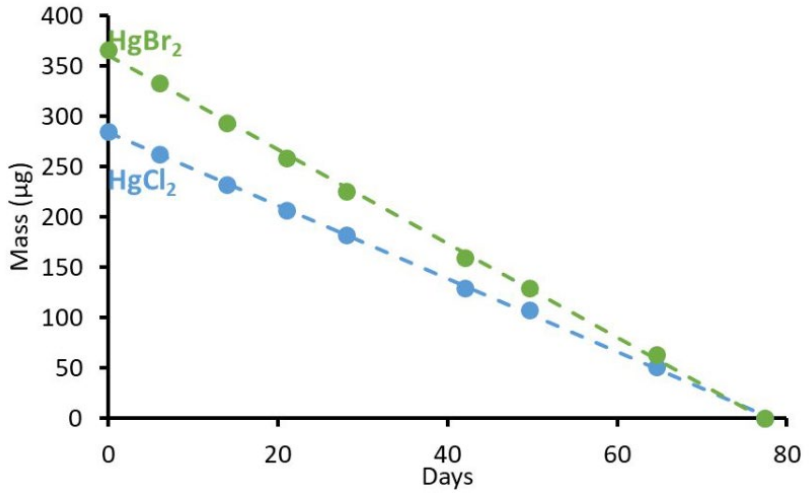


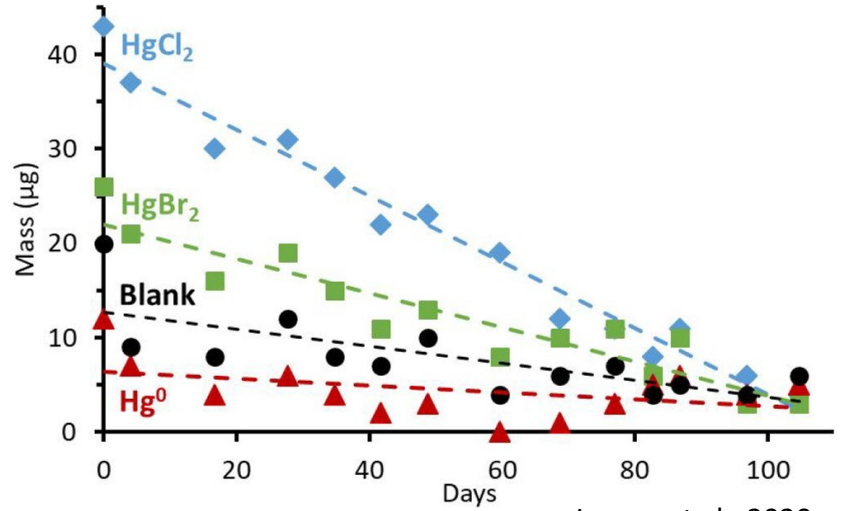
Basic principles of our method

- Tubes kept warm (50-70°C?), which keeps the permeation rate stable
- Permeable area minimized to keep permeation rate low
- Inert materials
- Give ample time for equilibration



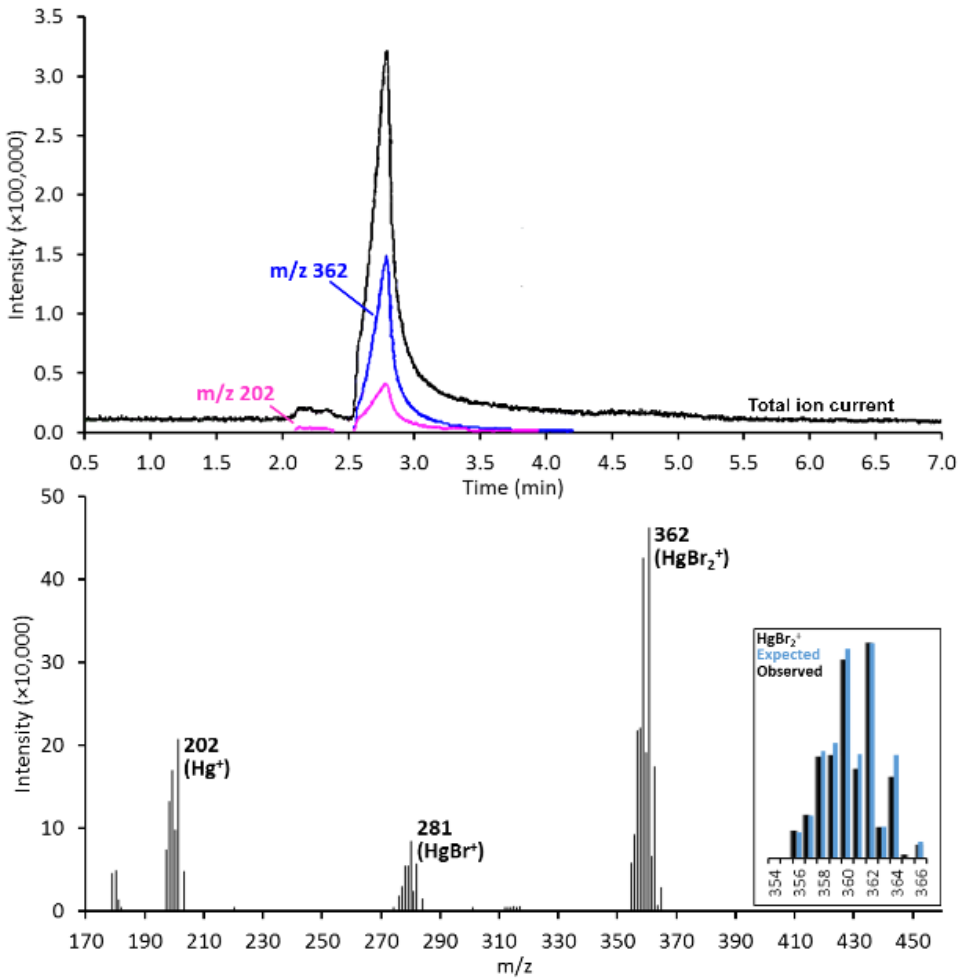
SI-traceable gravimetric verification of permeation rate





Lyman et al., 2020

Verification of chemical speciation by GCMS



Lyman et al., 2020; Jones et al., 2016

Recent success (Elgiar et al., 2024): Validation of SI-traceability

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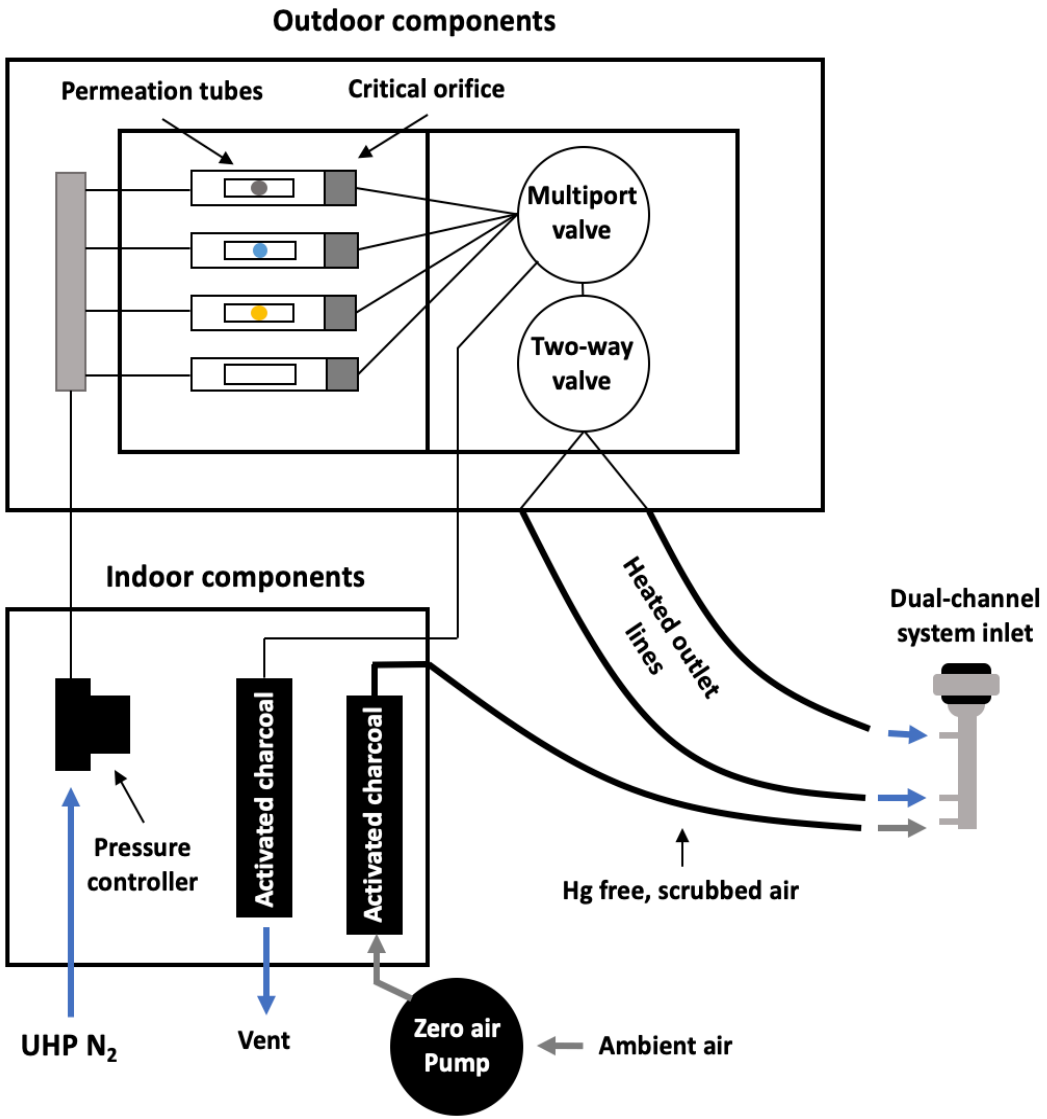
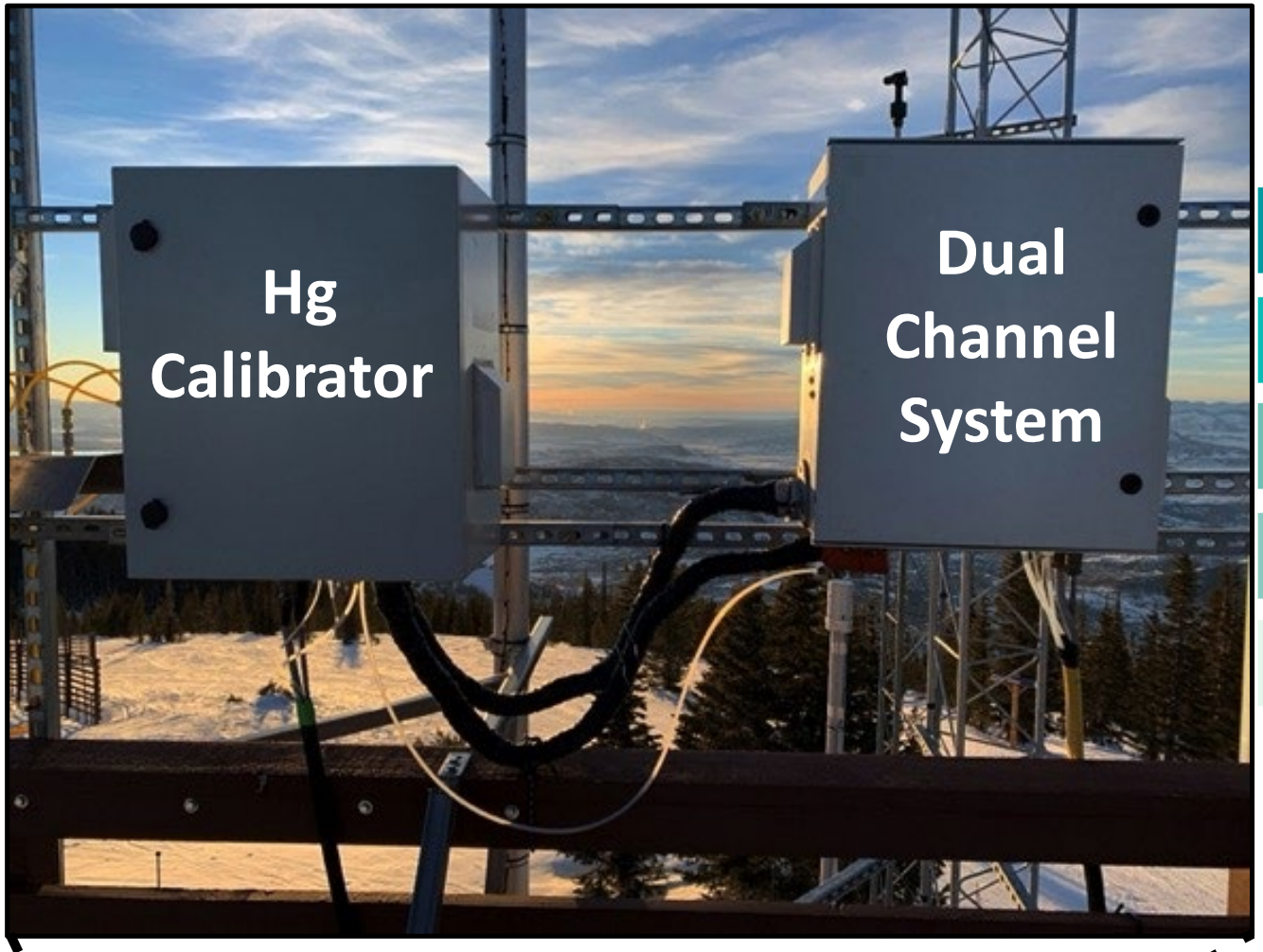
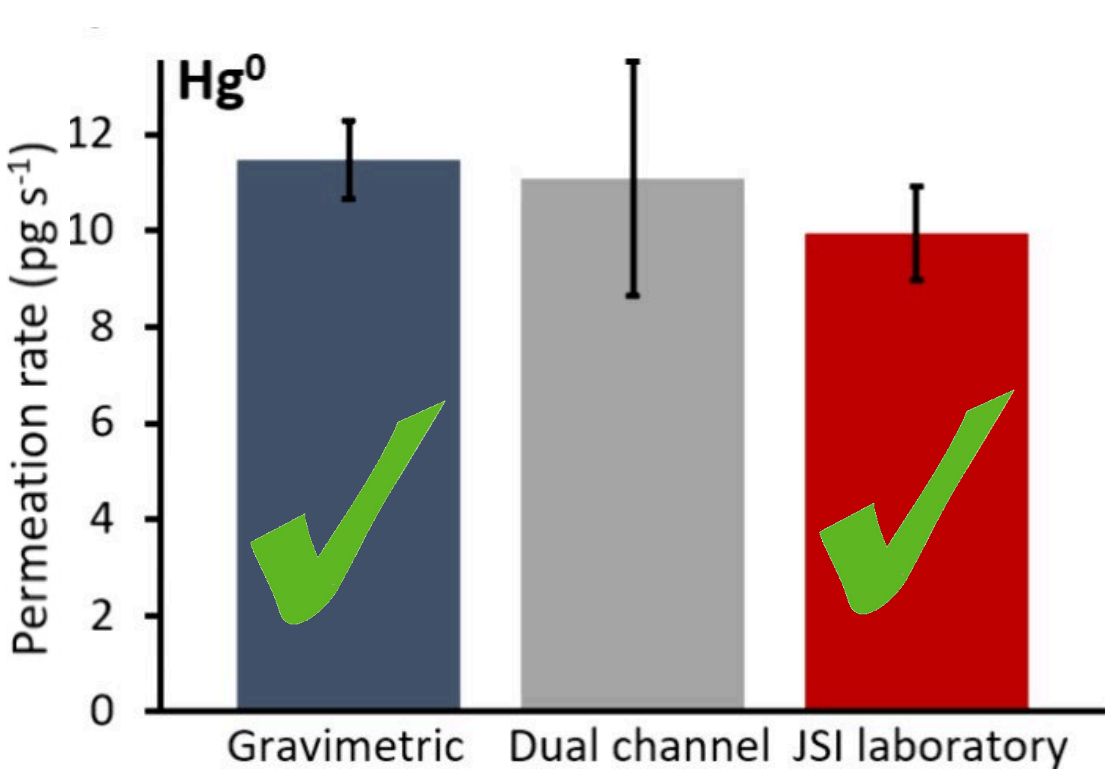
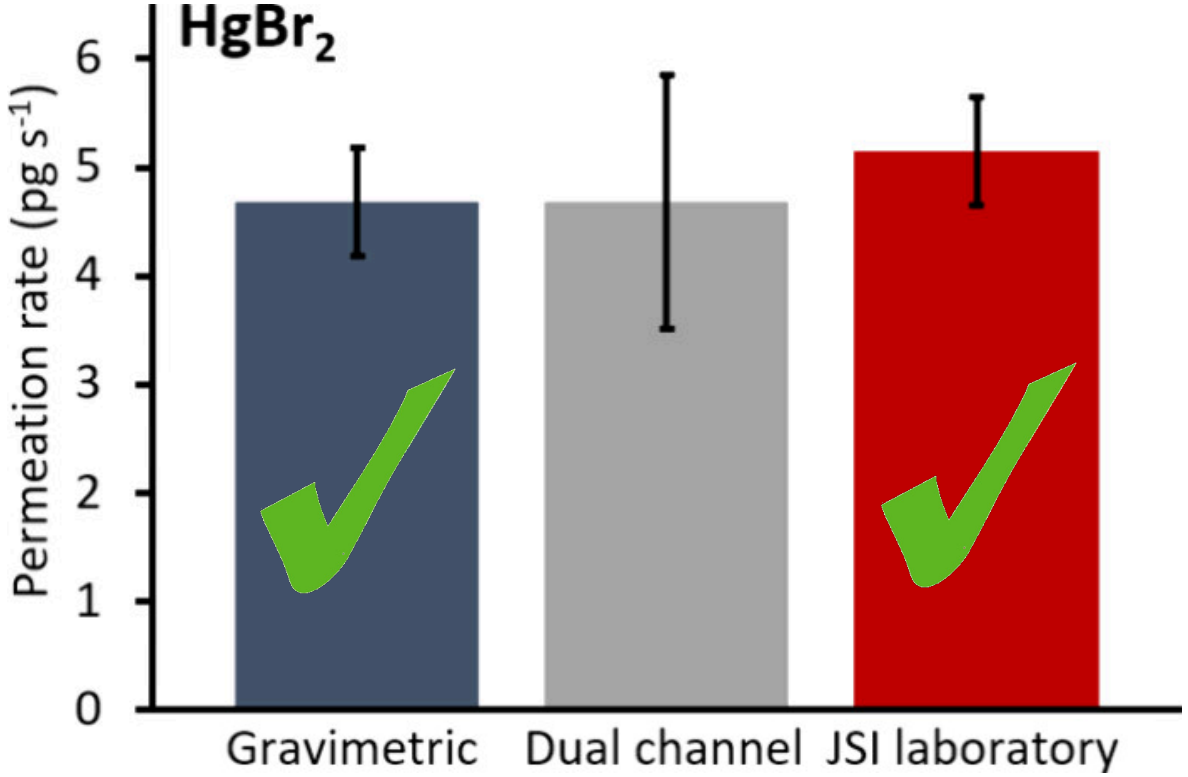




Recent success (Elgiar et al., 2024): Validation of SI-traceability





Remaining Challenge:
All available materials retain Hg compounds

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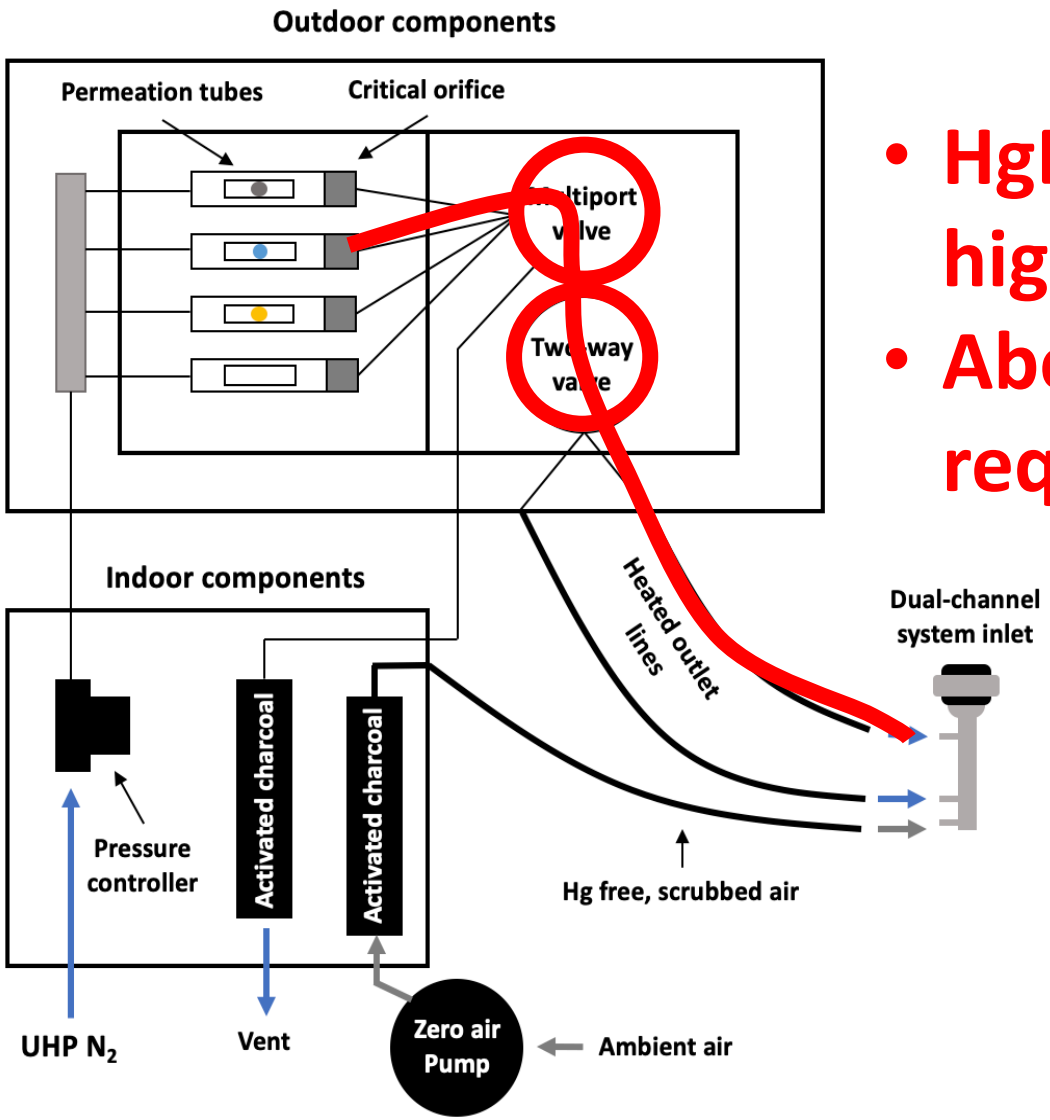

- $HgBr_2$ is retained by all surfaces, even at high temperature (up to 150°C)
- About 2 hours of continuous flow is required to achieve equilibration

Remaining Challenge:
The last centimeter

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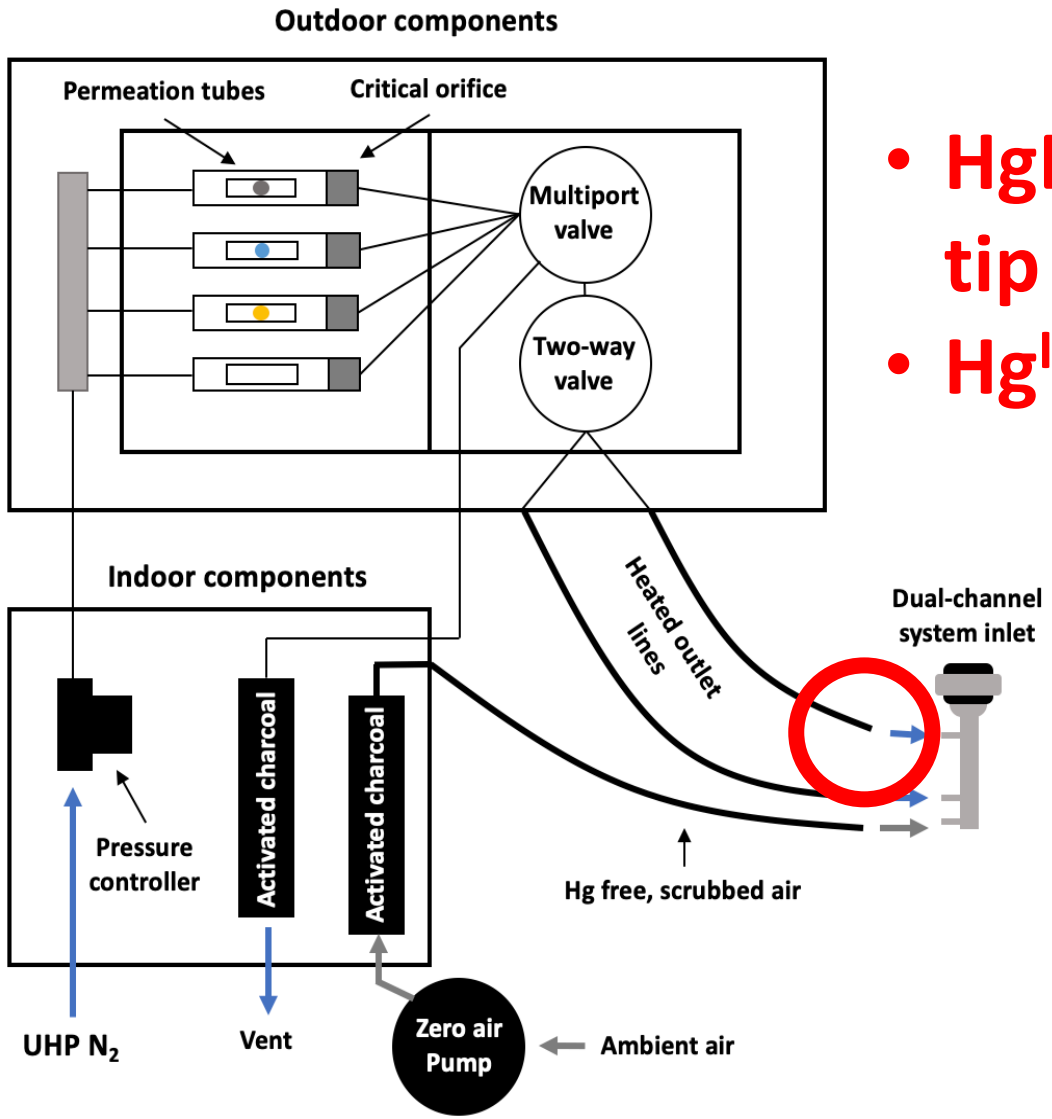

- $HgBr_2$ can be retained on unheated inlet tip
- Hg^{II} can spike when inlet is first inserted

Remaining Challenge: Stability/permeation rate tradeoff

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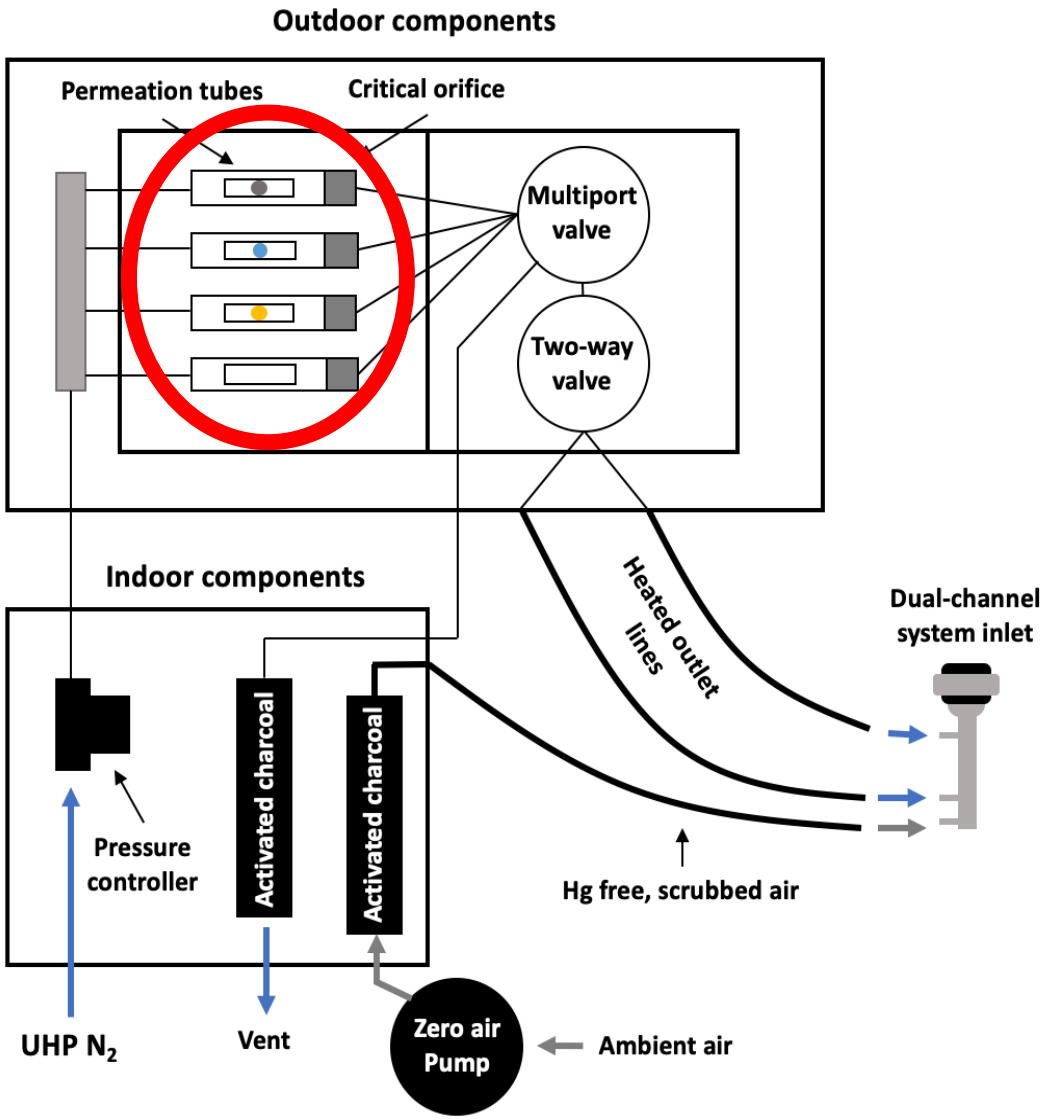

- Permeation rates are:
  - unstable at low temperatures (probably even at 50°C)
  - Too high at high temperatures
- Intermittent injection is difficult
- Dilution calibrators could work

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How to make speciation of output NIST-traceable?

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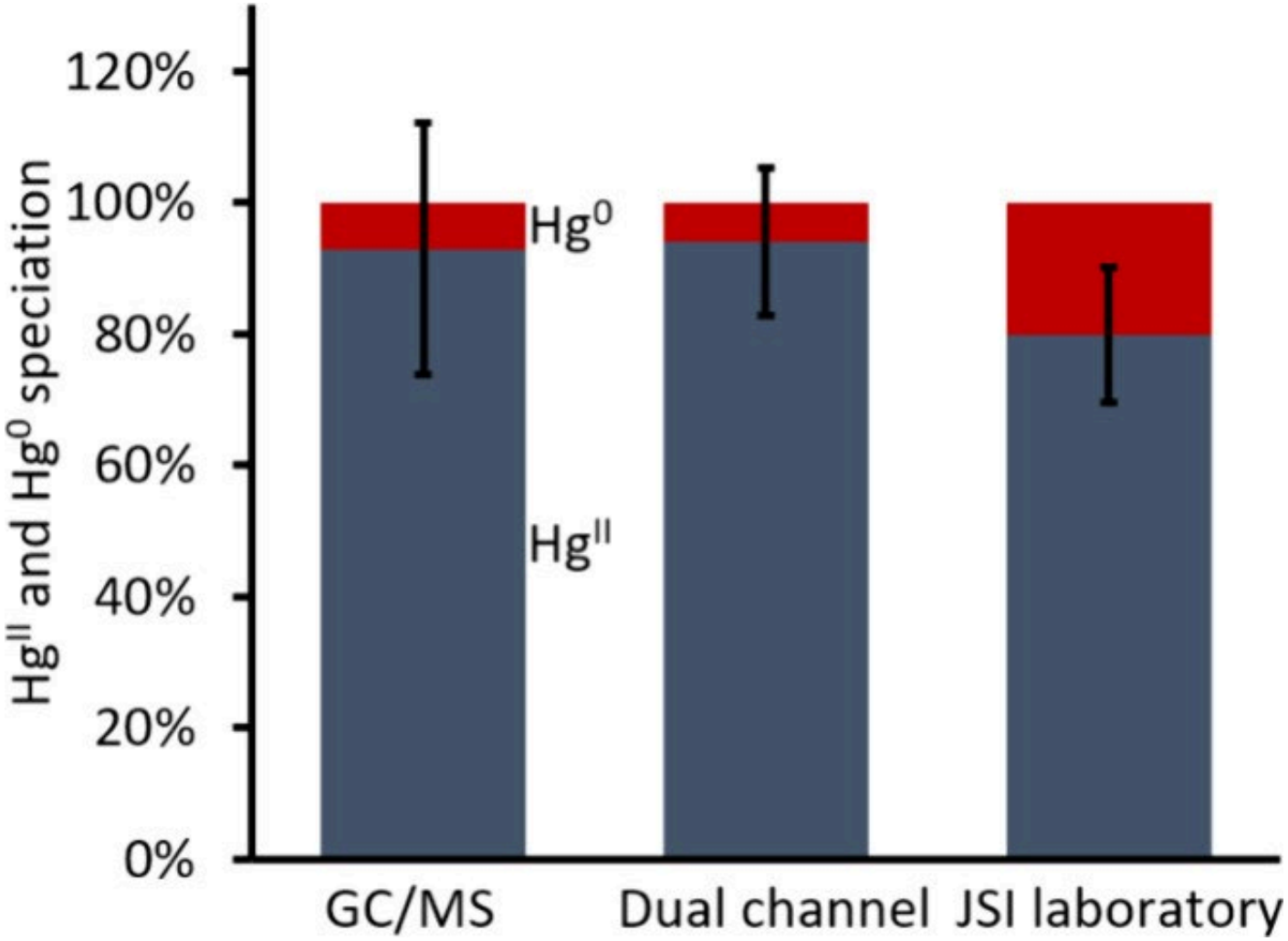

- **Our method results in some Hg^0 output**
- **Is there a traceable method to verify how much?**

From Elgiar et al., 2024

Remaining Challenge:
Will it work for non-halide Hg compounds?

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