Air Mercury Speciation Accuracy and Calibration

Presented at the

SFO Air Mercury Speciation Workshop

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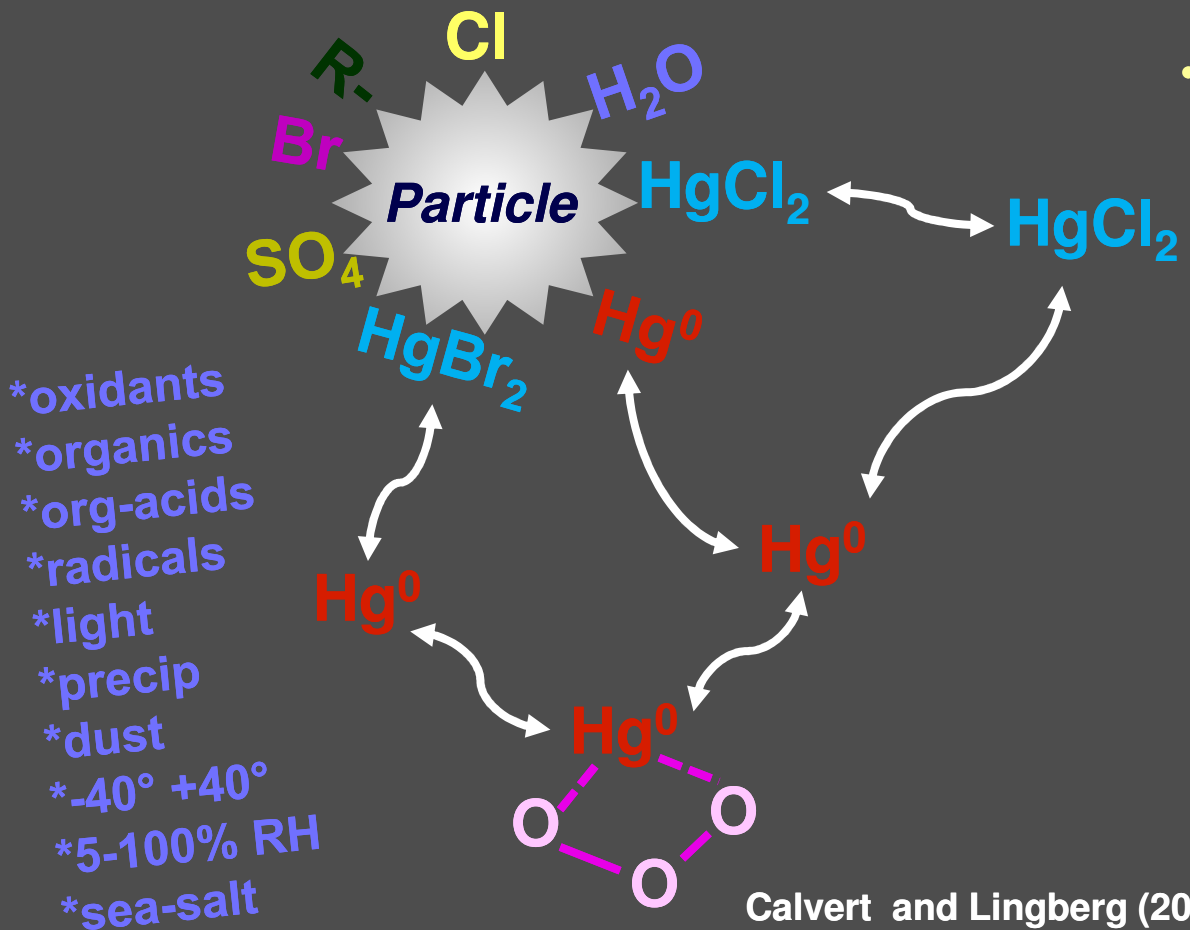


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How hard can it be to measure Hg speciation?

GOM & PBM ~ 1 ppqv

GEM ~ 170 ppqv



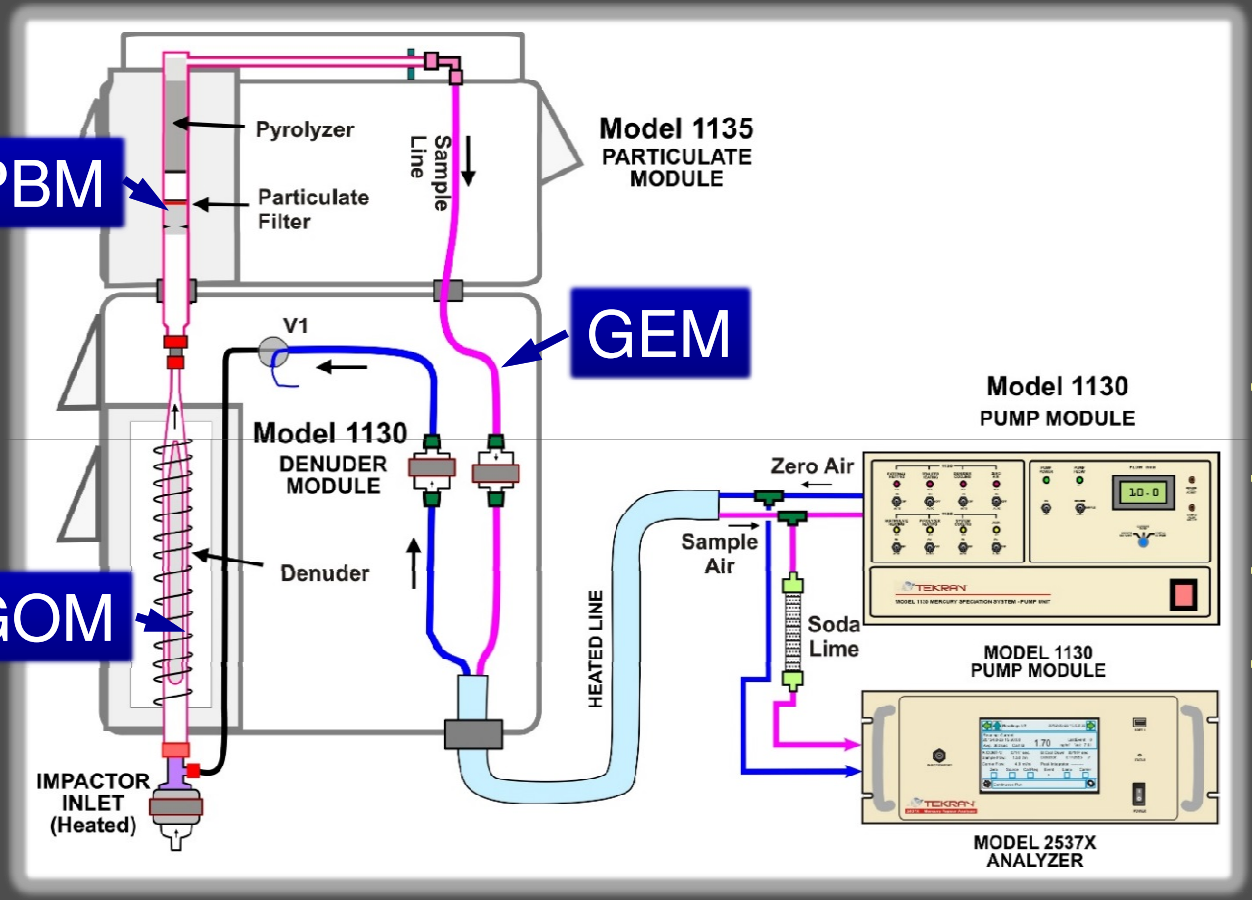
Calvert and Lingberg (2005)

- How likely is it that an automated atmospheric speciation system can automatically measure at the 1 PPQV (10 pg/m^3) level without any artifact bias in all types of atmospheres such as Arctic, urban Asia, free-trop, tropics, sub-tropics, marine, desert, etc.?

Q1: Is there a better way?

- Starting over, is there a better way to continuously measure GEM, $PBM_{2.5}$ and GOM with hourly resolution, 5 pg/m^3 (0.5 ppqv) DL and routine GEM and periodic GOM calibration?
- Conclusion – A 2.5 um inlet **>** annular denuder **>** particulate filter **>** gold-trap AFS is the only method that makes sense for the vast majority of ongoing and future scientific programs

Automated Hg Speciation Method (pat'd)





Method is:

- Lab tested
- Widely published
- QA Challenged
- Adopted by all advanced int'l & national networks

SIDEBAR

Historical Perspective for Atm. Hg Speciation Measurement

- **1994 GENESIS:** Small group of international experts convened and concluded that GOM should exist & method development must be a high priority (EPRI Report).
- **EARLY EXAMPLE:** 1996 at ICMGP – Report of unbelievable GOM levels of ~800 pg/m3 at Izania free troposphere site using manual filter pack method (Prestbo and Bloom). Is method biased?
- **DISCOVERY: 2000 -** Using automated Hg speciation method, Landis and many others* started reporting high GOM in the free troposphere and Swartzendruber et al. (2006) published the first peer-reviewed article.
  *Lyman, Jaffe, Obrist, Sheu, Feng, Slemr….

Select Hg Speciation Discoveries

- High GOM and PBM observations where reactive halogen chemistry is favorable
  - Polar Regions, Dead Sea, Free Troposphere, Marine Boundary Layer
- Elevated PBM/GOM from Biomass fires
- Confirmation of speciated mercury emissions from point sources
  - Coal Burning, Chlor-Alkali Plants & Waste Incinerators
- *Conclusion: Hg speciation measurements are scientifically coherent*

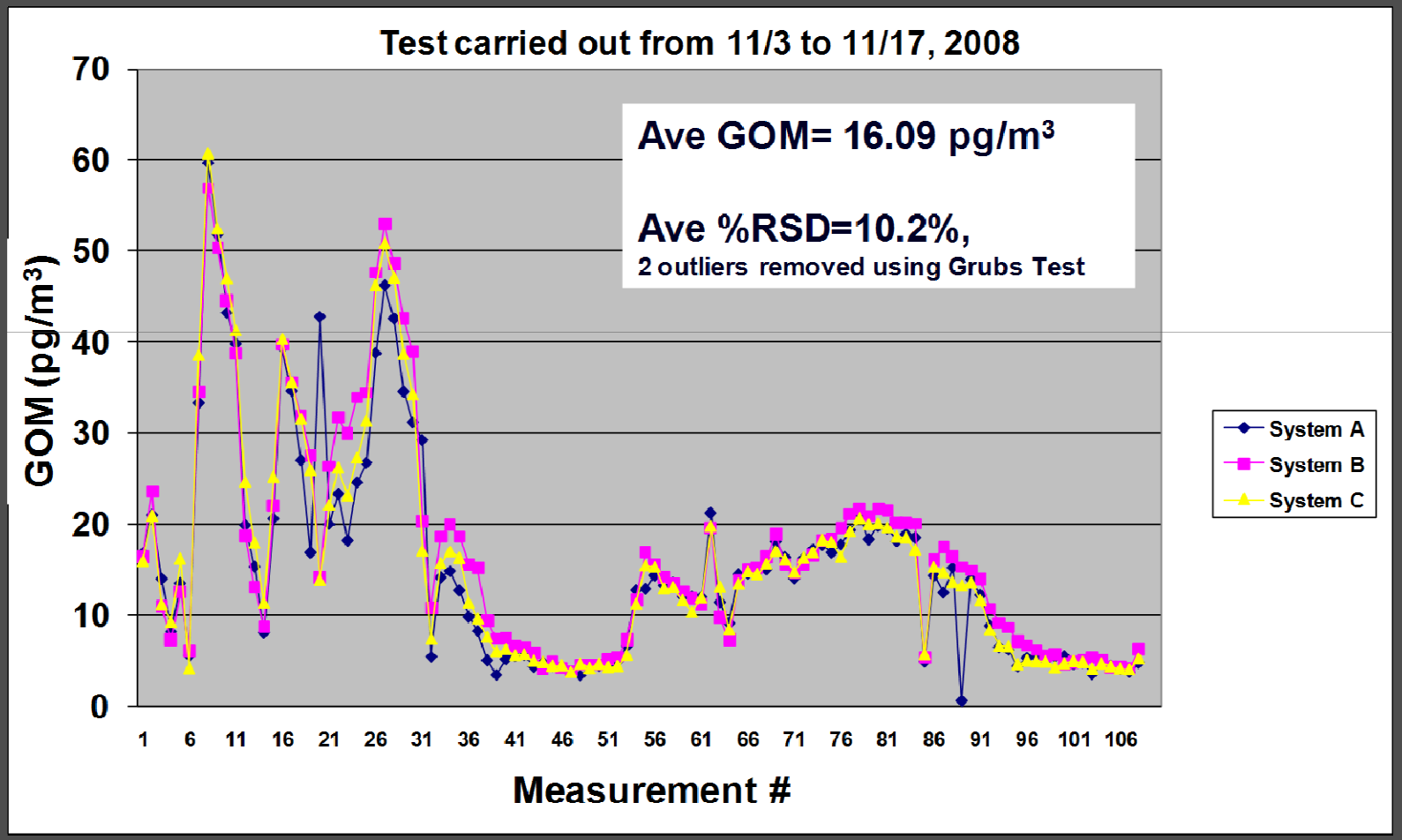
Two questions for the automated air mercury speciation method

- Scientists are asking:

- Exactly what is being measured?
- How accurate are the GOM and PBM measurements?

QA Challenge Example: GOM Manifold Comparison of 3 Tekran Systems

(See Olson et al., ICMGP-2013)

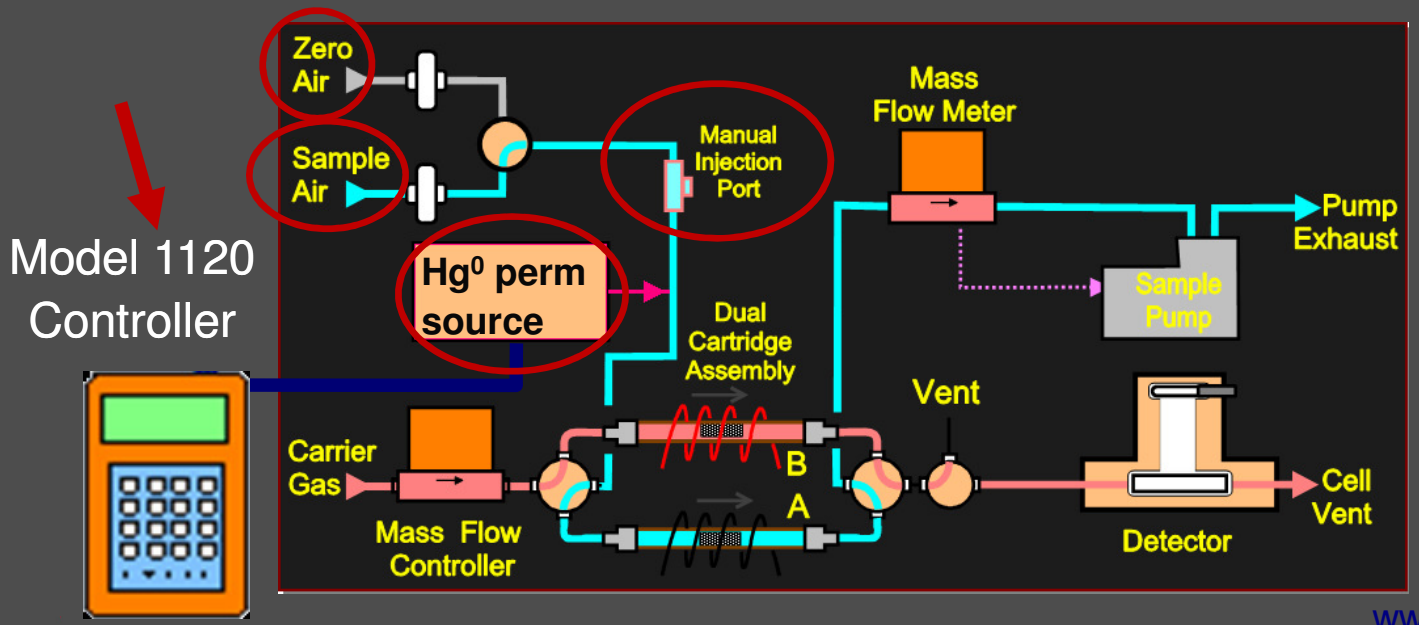


Side-Bar: Accuracy dependent on siting, operation, maintenance and QA

- 2007 Survey Says – experts rarely do external calibration and no audit of the sample volume measurement
- Inlet must be in free air with unobstructed large fetch
- Current and developing networks are improving the accuracy of Hg speciation measurements
  - CAMNet/CAPMoN, UBA-Germany, AMNet, GMOS, EMEP, AMAP, S. Korea, etc.

Traceable Hg^0 calibration and performance check options

- Automated calibration with permeation source
- Validation of permeation source at injection port
- Manual standard additions at injection port
- Automated perm source std. additions with 1120

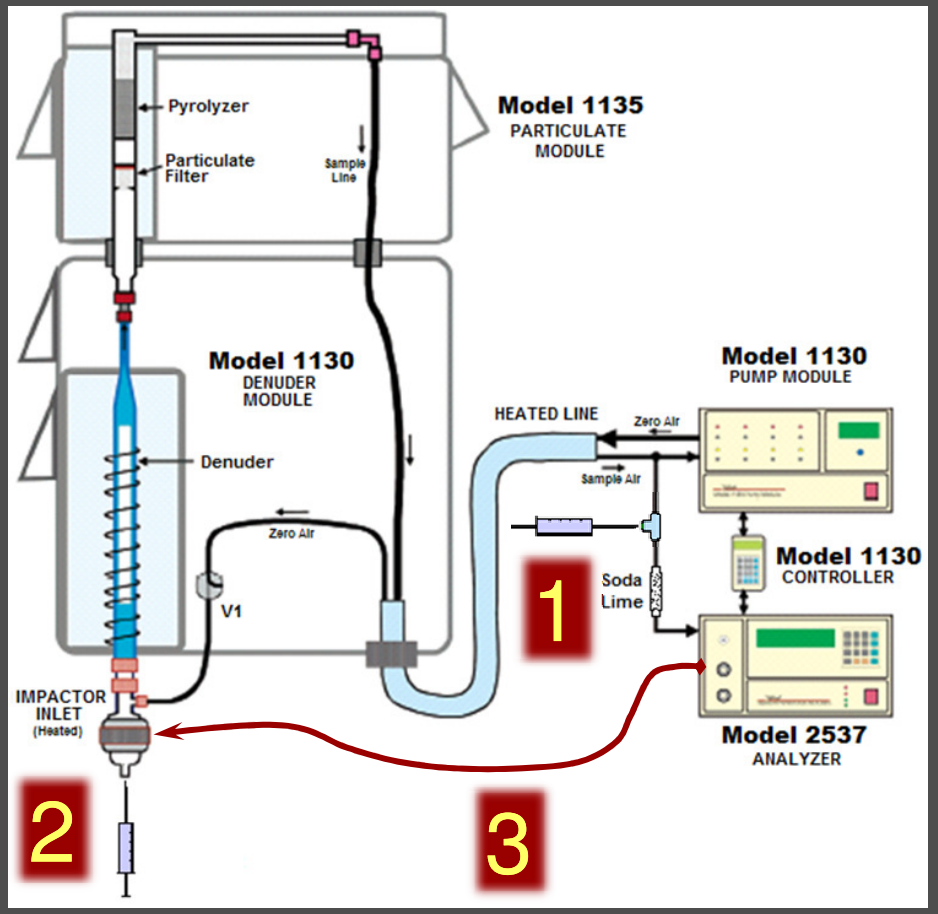


Model 1120 Controller

Model 2537 Schematic

Traceable Hg^0 fictive-loss test options
during ambient air sampling

1. Simple – manual Hg^0 injection upstream of the soda lime
2. Difficult – manual Hg^0 injection at 1130 inlet
3. Automated – proposed permeation source Hg injection at 1130 inlet



GOM Calibration Challenges

- $HgCl_2$ and $HgBr_2$ are solids at room temperature, so will adsorb to reactive and/or unheated surfaces
- Thus, quantitative transport requires optimization for laminar flow and short residence time (Tekran 1130 inlet and denuder) and/or brute force of high temperature through entire, non-reactive flow path (150-180º C)

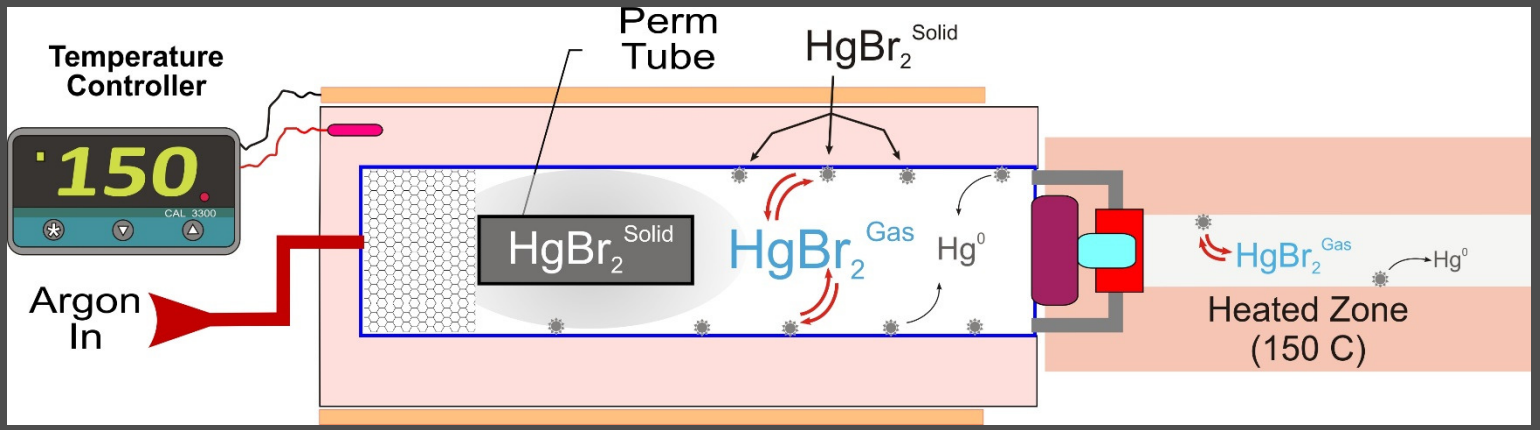
GOM Calibration Challenges

- $HgCl_2$ adsorbed to surfaces will convert to Hg^0, especially at high temperature or even changing air chemistry
- *parts per quadrillion* (10 to 500 picogram/m^3) concentrations required for calibration
- Source must be stable, reproducible, robust and can be turned on & off

Traceable Calibration of GOM Measurements

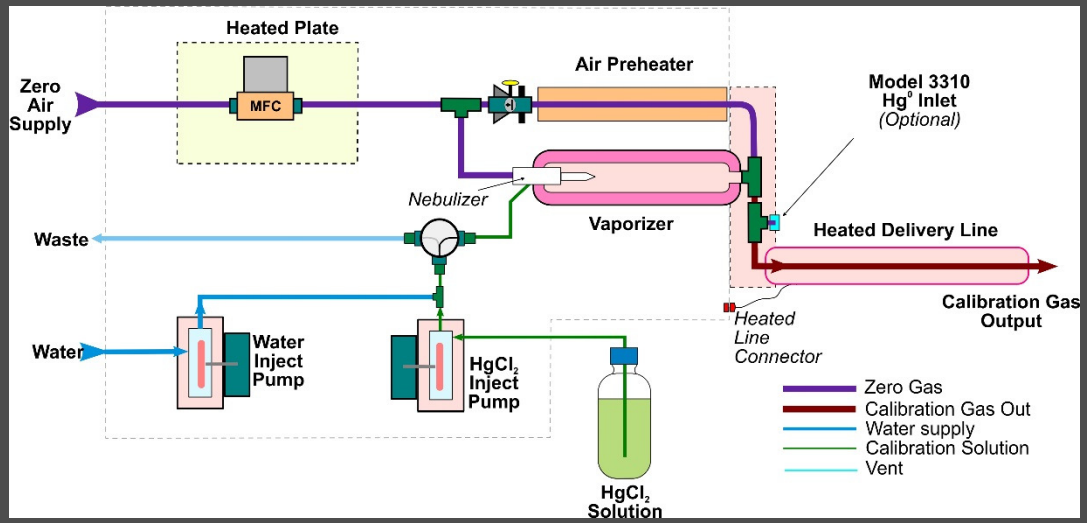
- Available Methods
  1. **Reaction** of traceable Hg^0 + 2 Cl > $HgCl_2(g)$ (catalyzed by reactive metal surface) Not 100% efficient
  2. Gas **permeation** of *pure* solid $HgBr_2$ to $HgBr_2$ gas (sublimation)
  3. **Nebulization** of NIST traceable standard $[HgCl_4]^{2-}$ solution
  4. **Manifold Spiking Research** – Ideally use independent NIST traceable GOM Source

The Trouble with Permeation for GOM Calibration



- **ADSORPTION:** Loss to surfaces in perm chamber or transport tubing (when off, cold spots) means device emission rate is a function of permeation and wall emissions.
- **STABILITY:** Wall losses in chamber or transport tubing, means that it can take weeks to stabilize or worse, the rate changes between uses
- **TEMPERATURE:** small changes in chamber or transport line temperature and/or humidity can cause big side-effects
- **CONVERSION:** $HgBr_2$ and $HgCl_2$ will convert to Hg^0 on surfaces

Nebulizing Liquid Hg Standard
Tekran Model 3315



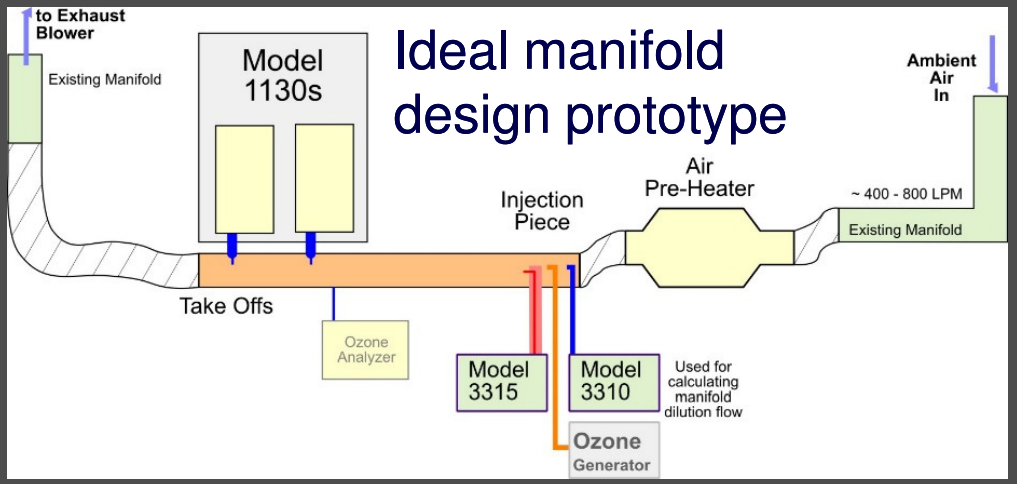
- Proven, traceable GOM source for HgCEM equipment QA
- Designed for 30 lpm and 1-40 ug/m^3

- Challenge is to modify device for delivery of GOM to the Tekran Model 1130 inlet at 1-15 lpm and 20 - 1000 pg/m^3.

Manifold Studies – RAMIX Comments

Gustin et al., doi:10.1021/es3039104

- Manifold studies to assess GOM and PBM accuracy are challenging and have a high degree of risk.



- The ideal manifold study would use GOM and GEM generators that are NIST traceable and independent of the measuring equipment being evaluated. RAMIX used a GOM permeation source, calibrated by the same equipment being evaluated.

Manifold Studies – RAMIX Comments

Gustin et al., doi:10.1021/es3039104

- GEM measurements did not agree using 2 highly QA'd identical Hg speciation instruments (Tekran) connected to the RAMIX manifold. *A 30% fudge factor was applied to correct this experimental bias.*
- GEM comparisons with two fully QA'd Hg speciation instruments are nominally better than 5%. GOM is nominally 10%.

Manifold Studies – RAMIX Comments

Gustin et al., doi:10.1021/es3039104

- Non-standard setup. 1.5 meters of inlet line & 4 lpm flow rate for the Tekran Hg speciation equipment. Transport losses and species conversion likely, but not tested.
- Lab manifold tests were done on a ¼ length of the field manifold. Lab tests showed uncertainty and less than 100% transmission efficiency for GEM & GOM. Flow uncertainty was +/- 15%
- Unusual results were explained by hypothesizing that GOM was generated in the manifold.

Conclusions

- Determination of accuracy for GOM and PBM at the parts per quadrillion level are difficult, but badly needed
- The Tekran 3315 modified for ambient levels may be the best option for field-based GOM accuracy determination. Tekran needs willing partners and funding to implement.
- Manifold studies for accuracy are difficult to do and prone to have their own artifacts

Q2: What does the consensus of the research & monitoring community need to improve "accurate" Hg speciation measurements, at high resolution, with a commercially available and supported system?

1. Current 2537-1130/1135 system, with modifications to improve accuracy & robustness and add a GOM calibration source?
2. A system that switches a 2537 between a GEM and $TAM_{2.5}$ mode, with the difference being a function of [GOM+$PBM_{2.5}$ + $V_{GEM\text{-}PBM\text{-}GOM}$], where $V_{GEM\text{-}PBM\text{-}GOM}$ is the natural variability of these species over the 5 to 10 minute time cycle of measurement. Est. DL of 100 pg/m^3 and 30% uncertainty?
3. A UW - DOHGS type system with two Tekran 2537 Units measuring $TAM_{1.0}$ and GEM simultaneously, including a GOM calibration source. Est DL of 50 pg/m^3?
4. Other?

Tekran future contributions to improve GOM/PBM automated method

- Prestbo would be willing to ask Tekran to contribute a large amount of in-kind resources to an acceptable, funded research project to develop modifications and new calibration sources for the 2537-1130-1135 system.
- Open invitation…..
- The size of the problem seems to require a coordinated, funded contribution from a larger community of atmospheric Hg experts ……