Accelerated test method to quantify changes in the composition of CO_2/air reference gases in cylinders

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nor does it imply that it is the best available for the purposes described.

Introduction … Motivation

- Importance of Reference Materials for monitoring of trace gases in atmosphere

Gas cylinders containing air with certified amounts/fractions of some trace gas(es)

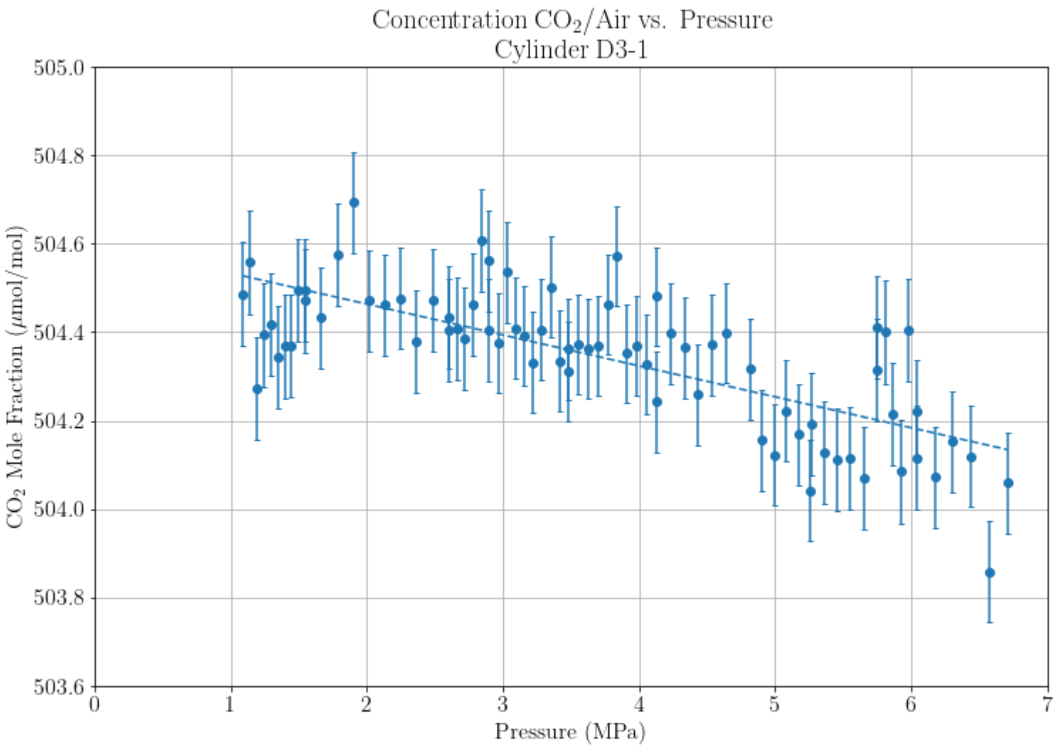
- RM Gas Cylinders suffer from a known issue: trace gas mole fraction changes as the cylinder is drawn down

- DQO by WMO: 0.1 and 0.05 µmol/mol

Heuristic Solution: Discard cylinder at some “low” p

- Exemplar: Trace CO_2 in synthetic Air

- Questions: What is “low” p? Alloy effects? Surface treatment effects?


Concentration CO_2/Air vs. Pressure
Cylinder D3-1

CO_2 Mole Fraction monitored while slowly drawing down pressure over the course of two months.

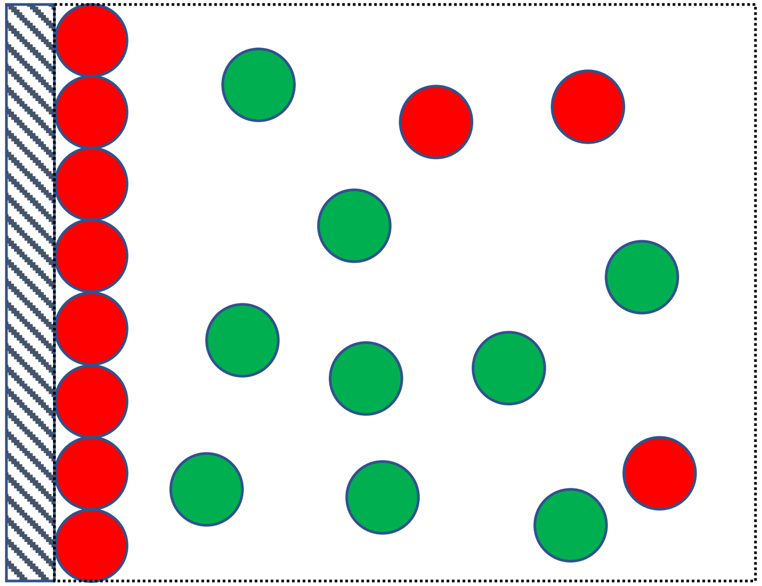
0.5 µmol/mol rise in CO_2 mole fraction

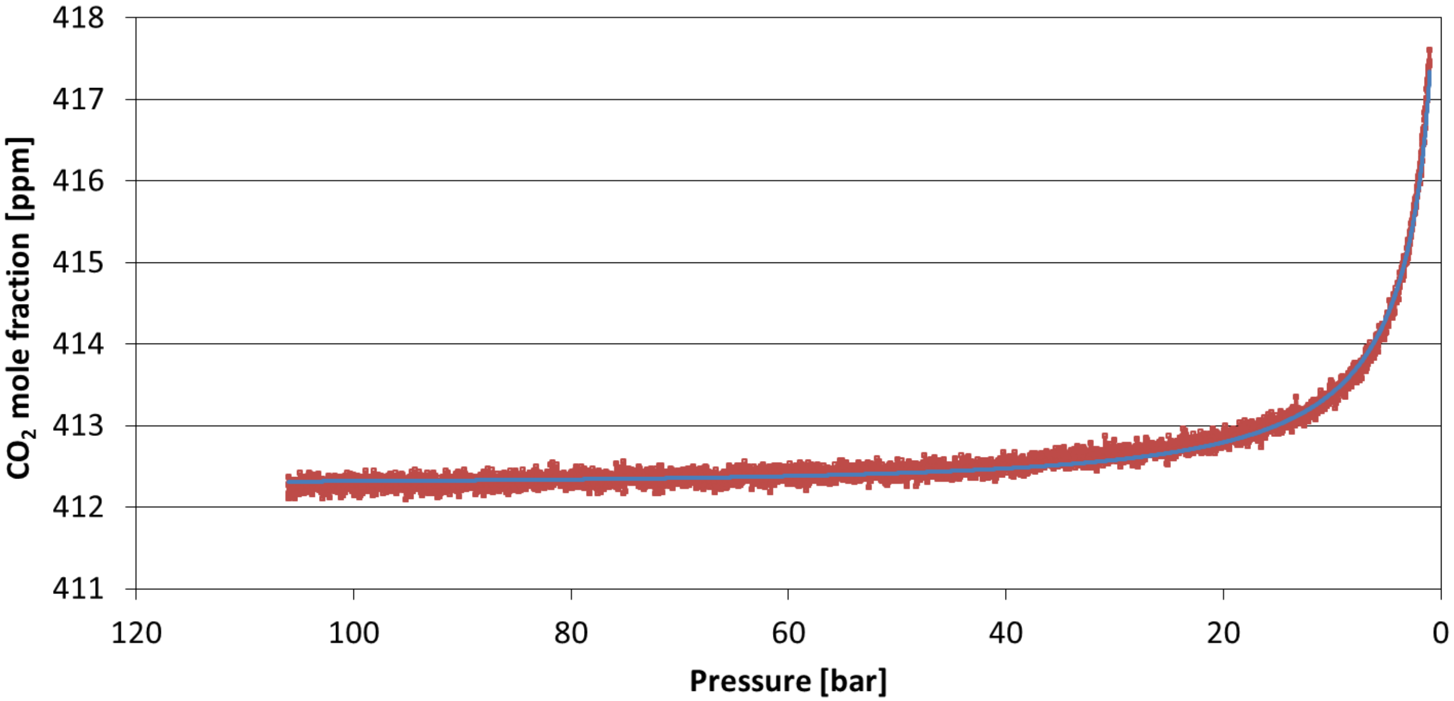
Consistent with Adsorption/Desorption

Leuenberger et al (2015): Model of composition change versus pressure:

1. CO_2 loss follows Langmuir Isotherm (Type 1)
2. No mass-transfer resistances
3. Slow decant, for temperature stability
4. Steel, Aluminum cylinders
5. CO_2, CH_4, CO

$$\Gamma_i = \Gamma^{\infty} \frac{K_i\, p_i}{1 + K_i\, p_i}$$

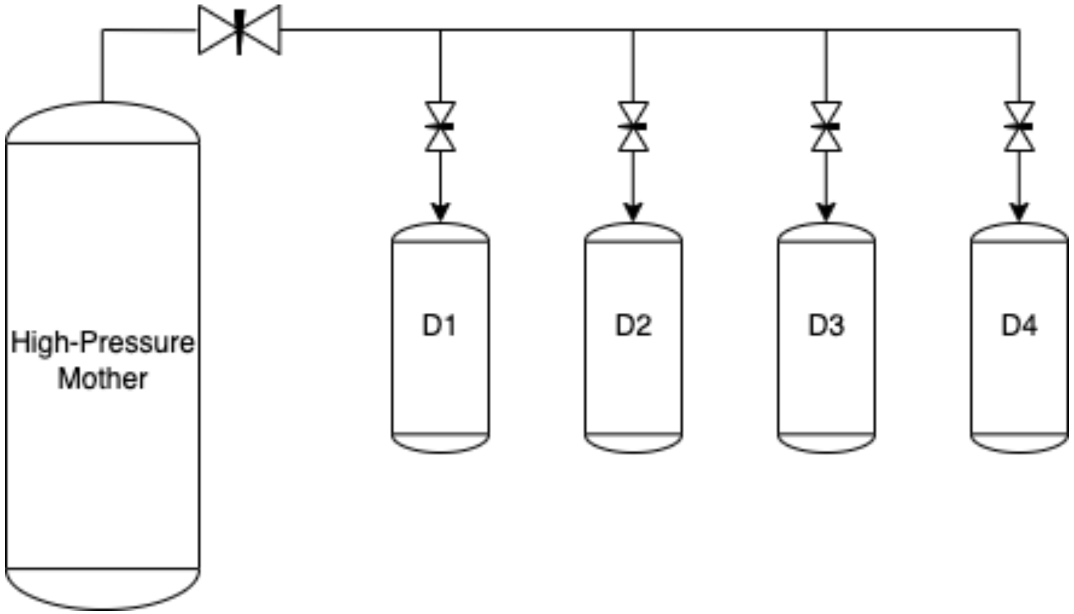


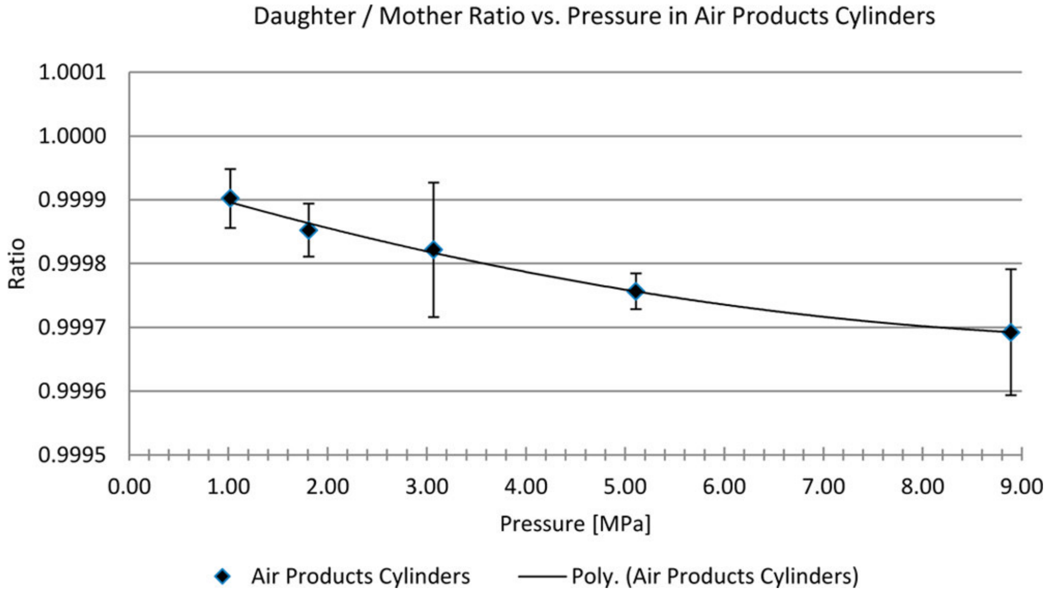


From: Leuenberger, Schibig, and Nyfeler, *Atmos Meas Tech* (2015)

CO_2 in Air, tempered steel cylinder (34CrMo4) 295 K

Mother/Daughter Generation Tests





From: Miller, Rhoderick, Guenther, *Analytical Chemistry* (2015)

CO_2 mole fraction ratio (rel. to mother) in Alum. cylinders

1. High-pressure “mother,” initial 390 µmol/mol CO_2 amount fraction
2. Transfer from mother to “daughters” until pressure and temperature equilibrium established
3. Composition analysis by Cavity Ring-down Spectroscopy, comparison of mother to daughters

   NOTE: Mother composition re-analyzed periodically against NIST primary standard mixtures
4. Repeat 2-3 to progressively draw down the mother

Observation:

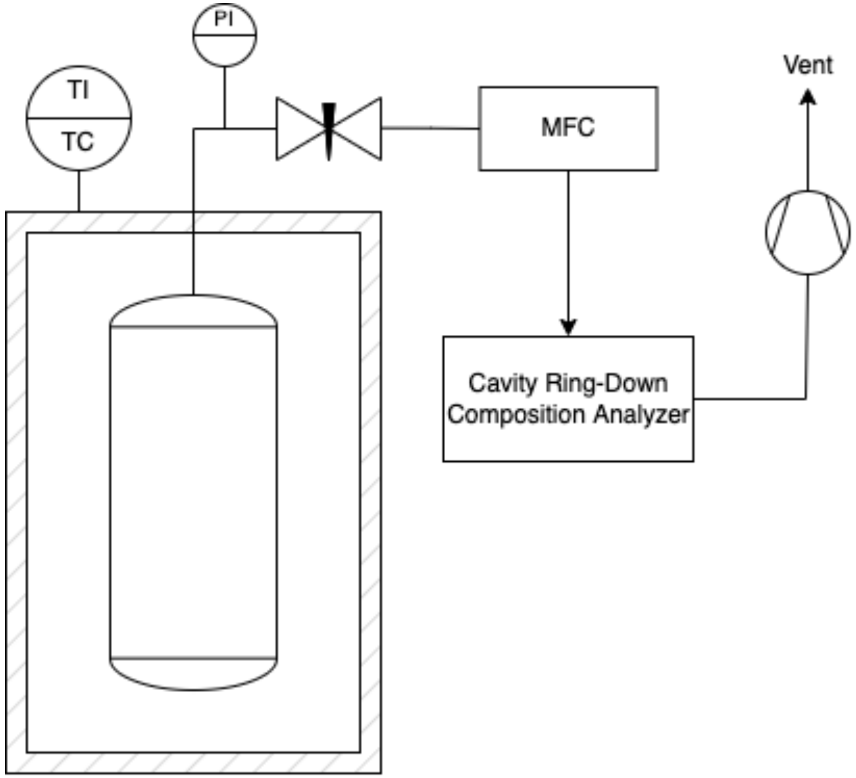
Highest pressure daughter shows most CO_2 “loss”

Consistent with adsorption hypothesis

Objectives of Present Work

- Building an experimental apparatus to decant cylinders faster than normal use. **Accelerate controlled analysis of cylinders**
- Improve theoretical model of cylinder discharge, include adsorption without mandating a particular equilibrium form. **Multiple adsorbing species**
- Use the experimental results in tandem with the improved model to gain understanding of the limitations and factors critical for improving measurements.
- Measurements/modeling guide extended life of RM cylinders, fast and robust prediction of cylinder behavior, suggest (rule out) mechanism(s) for composition changes

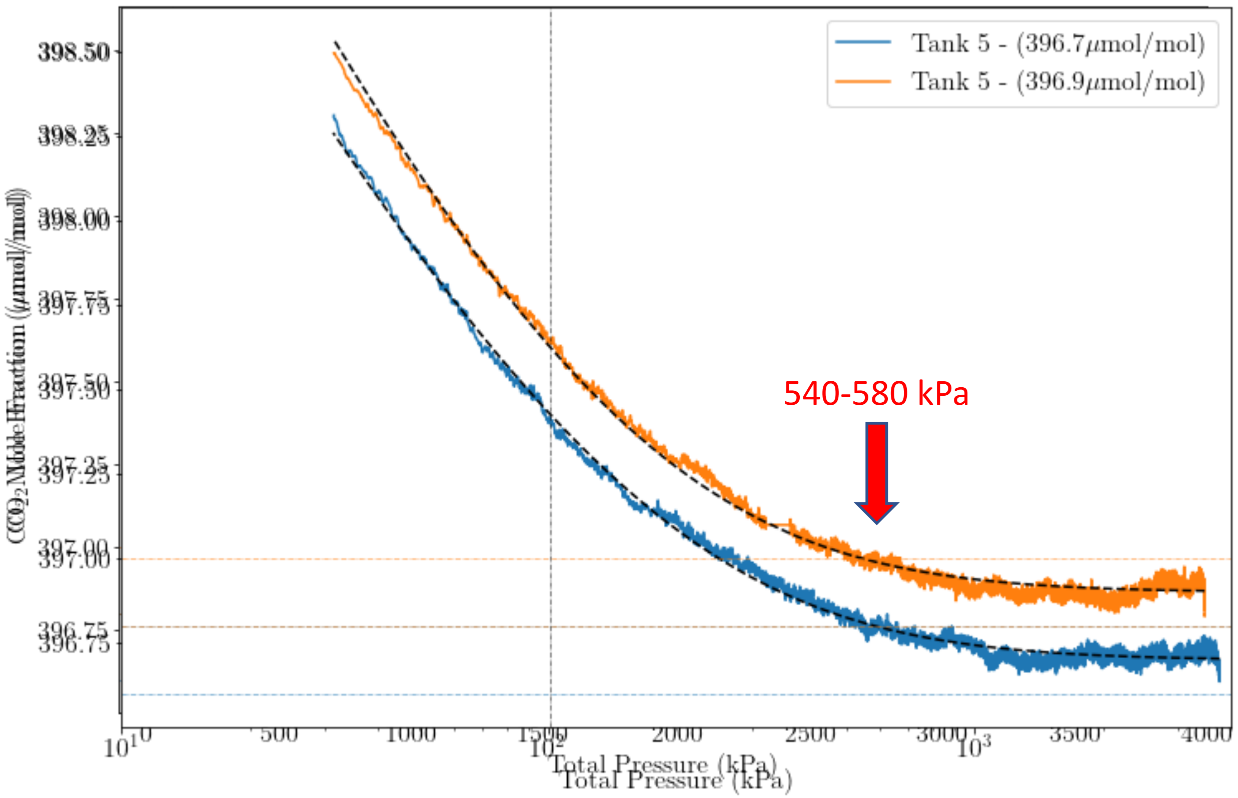
Experimental Apparatus



- Temperature-stabilized cylinder chamber for extended measurements and control **(stable over duration of experiment)**
- Multiple pressure sensors and controllers. **Pressure dynamic range from 3.5 MPa to 34 kPa.**
- Sensitive Mass flow controllers **(for measurement precision and accuracy)** [0.015 l/min (STP)]
- Impurity analysis and reduction **(Turbomolecular pumping system, manifold purging, and low temperature baking to remove water)**
- Use of spectroscopic techniques with excellent stability, repeatability, reproducibility. **Cavity ring-down spectrometer and other ex-situ instruments with sensitivities in very low amount fractions**
- **FAIR** Data Acquisition: Use standard formats, like the Adsorption Information Format (IUPAC)

Experimental Results

Leuenberger, Schibig, and Nyfeler, *Atmos Meas Tech* (2015)



540-580 kPa

Aluminum Alloy Cylinder, CO_2 in Air

Decant cylinder over 7-8 days

1) Leuenberger model fits the observed trend

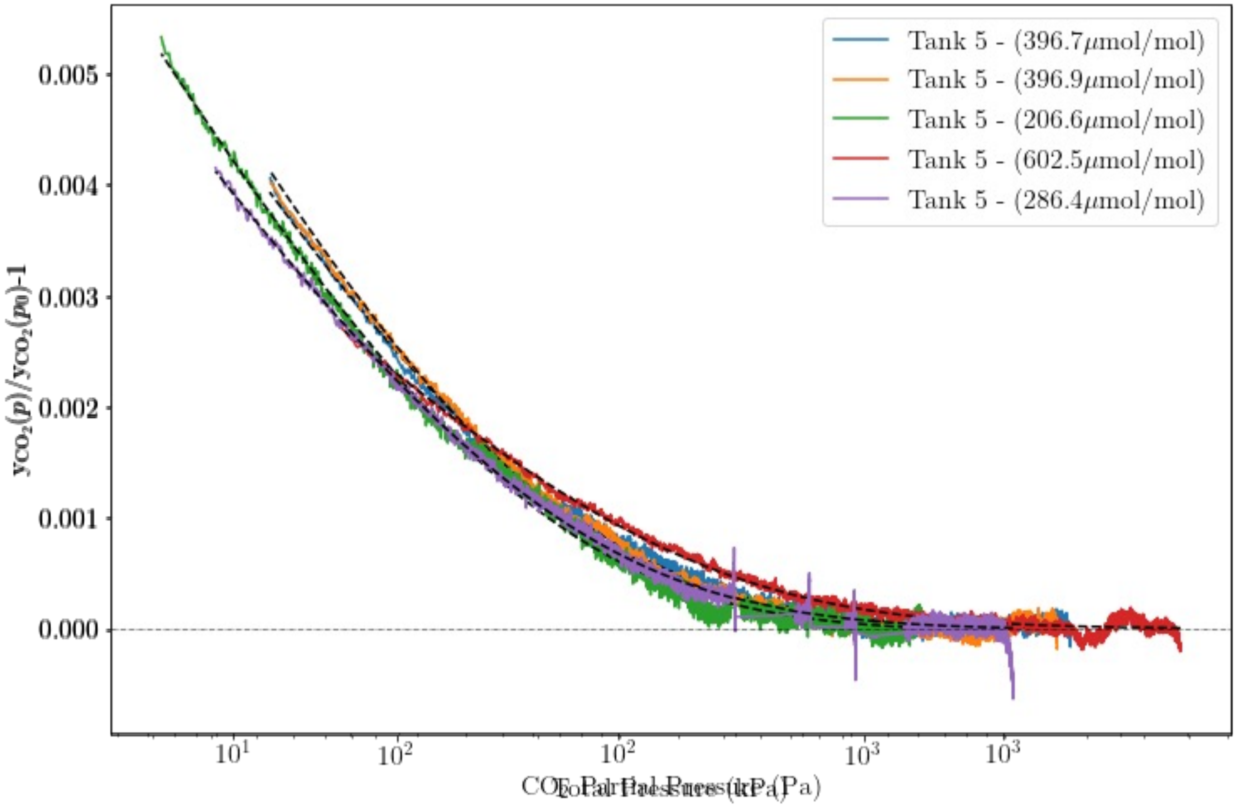
2) Model estimation of “adsorption excess” relative to bulk phase CO_2

	396.7 µmol/mol	396.9 µmol/mol
K (equilibrium constant)	0.0066 1/Pa	0.0079 1/Pa
Half pressure	151 Pa	124 Pa
95% max loading	2860 Pa	2418 Pa
Rel. adsorption excess	2.4e-10	2.5e-10

$$\text{Excess} = \frac{\Gamma_i(p_{i,0})A}{N_{b,i,0} + \Gamma_i(p_{i,0})A} \approx \frac{(\Gamma^\infty ART/V)}{y_{i,0}\, p_0}$$

Consistency with Leuenberger Model

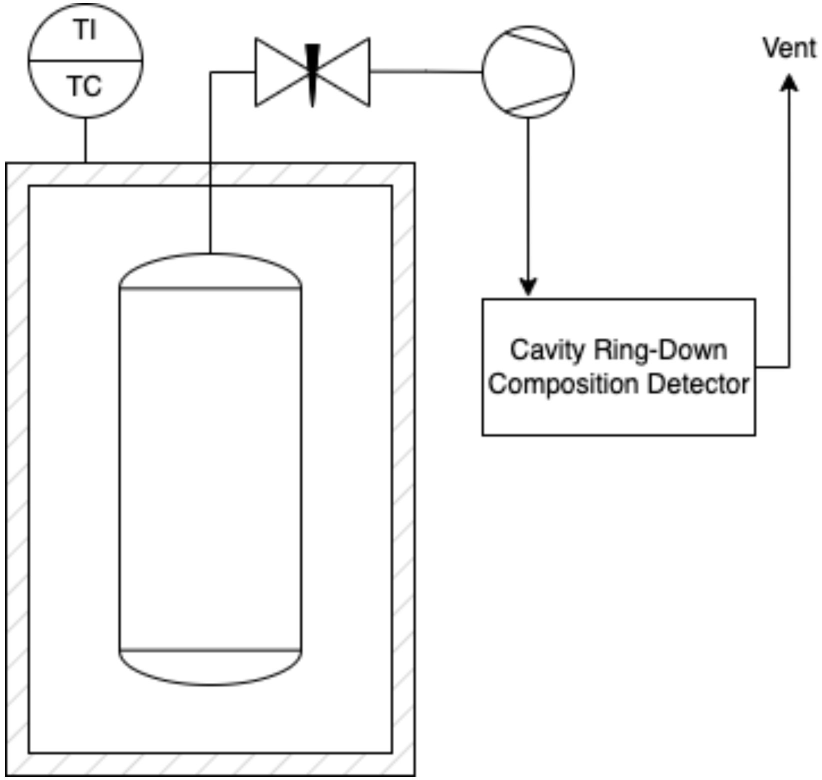
Leuenberger, Schibig, and Nyfeler, *Atmos Meas Tech* (2015)



- Measurements consistent with Leuenberger model for range of pressures of compositions
- "Master curve" when plotted versus CO_2 partial pressure; model can be written in approximate form

$$\frac{y_i(p)}{y_{i,0}} - 1 = -K_i\left(\frac{\Gamma^\infty ART}{V}\right)\left(\ln\frac{K_i y_{i,0} p}{1 + K_i y_{i,0} p} + \frac{1}{1 + K_i y_{i,0} p}\right) \approx -K_i\left(\frac{\Gamma^\infty ART}{V}\right)\left(\ln\frac{K_i p_i}{1 + K_i p_i} + \frac{1}{1 + K_i p_i}\right)$$

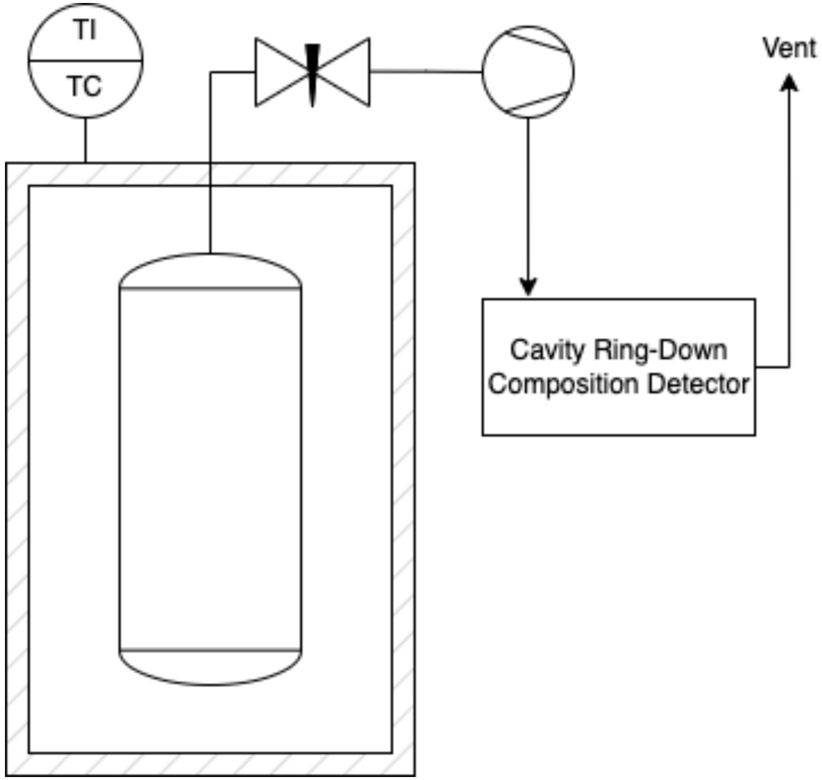
Improved Cylinder Discharge Model



Mass Balance	$N_i = N_{b,i} + N_{a,i} = \frac{p_i V}{RT} + \Gamma_i(\{p_1, \cdots, p_m\})A$
Loss Function	$\frac{dN_i}{dt} = -y_i \dot{N}$ where $y_i = \frac{N_{b,i}}{\sum_m N_{b,m}} = \frac{p_i}{p}$
Adsorption Constraint	Interchangeable
Other	Isothermal (no heat/energy balance) Normalize extensive quantities by *V*
Solution Method	Euler integration, stop/start equilibrium [forward propagation, recompute EQ conditions, repeat]

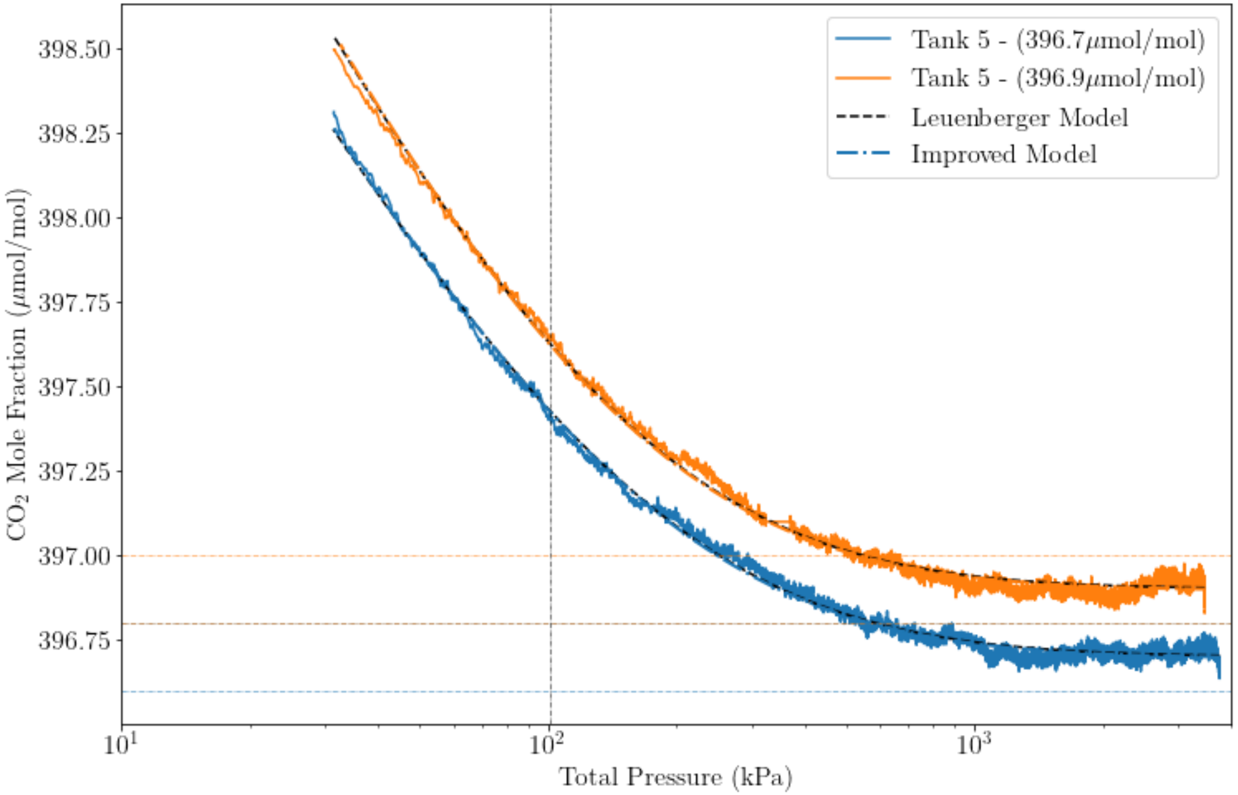
Key Changes: Solution is for *mass (mol)* quantities; agnostic to adsorption model.
“Down side”: Numerical solution (vs. analytic Leuenberger)

Improved Cylinder Discharge Model



Mass Balance	$N_i = N_{b,i} + N_{a,i} = \frac{p_i V}{RT} + \Gamma_i(\{p_1, \cdots, p_m\})A$
Loss Function	$\frac{dN_i}{dt} = -y_i \dot{N}$ where $y_i = \frac{N_{b,i}}{\sum_m N_{b,m}} = \frac{p_i}{p}$
Adsorption Constraint	Traditional Langmuir: $\Gamma_i \cdot \frac{A}{V} = \left(\frac{\Gamma^\infty A}{V}\right) \frac{K_i p_i}{1+K_i p_i}$
Other	Isothermal (no heat/energy balance) Normalize extensive quantities by *V*
Solution Method	Euler integration, stop/start equilibrium [forward propagation, recompute EQ conditions, repeat]

Improved Model: Consistency Check

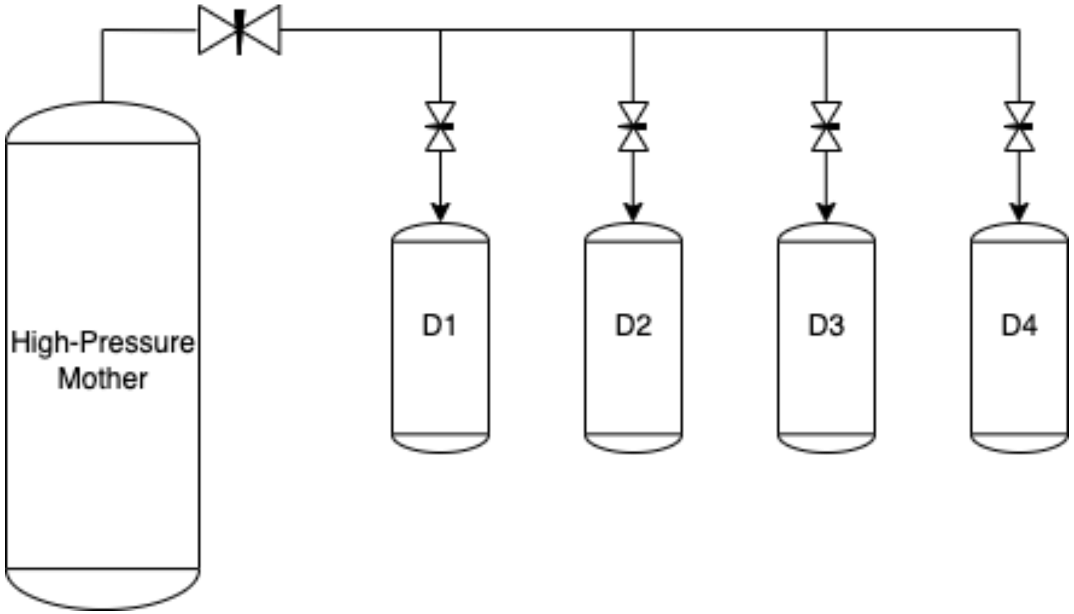


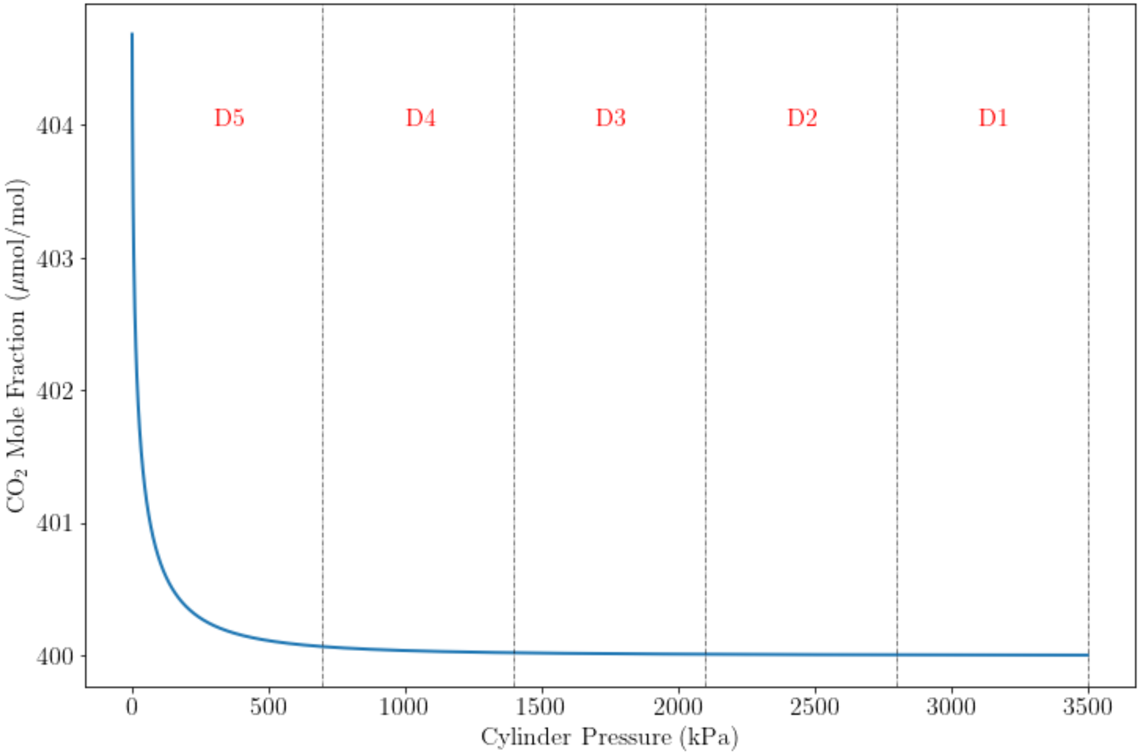
- Improved model essentially identical to Leuenberger model ***for single adsorbing species***

- New questions:
    - Mother/daughter modeling
    - Sensitivity to fitted parameters

- NOTE: Approximate analytic solution available, not used

Mother/Daughter Generation Tests





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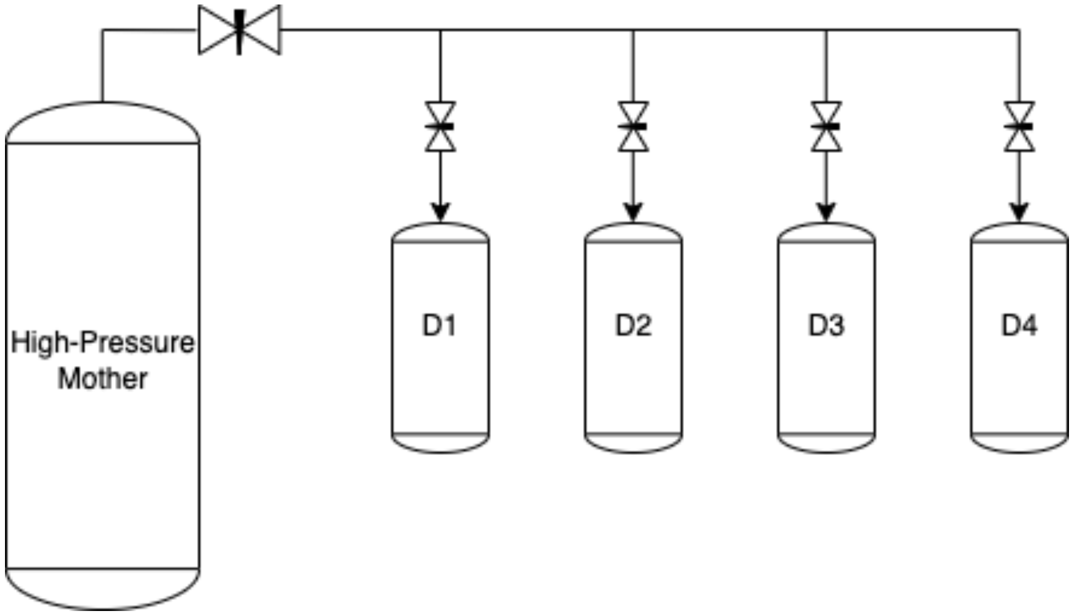
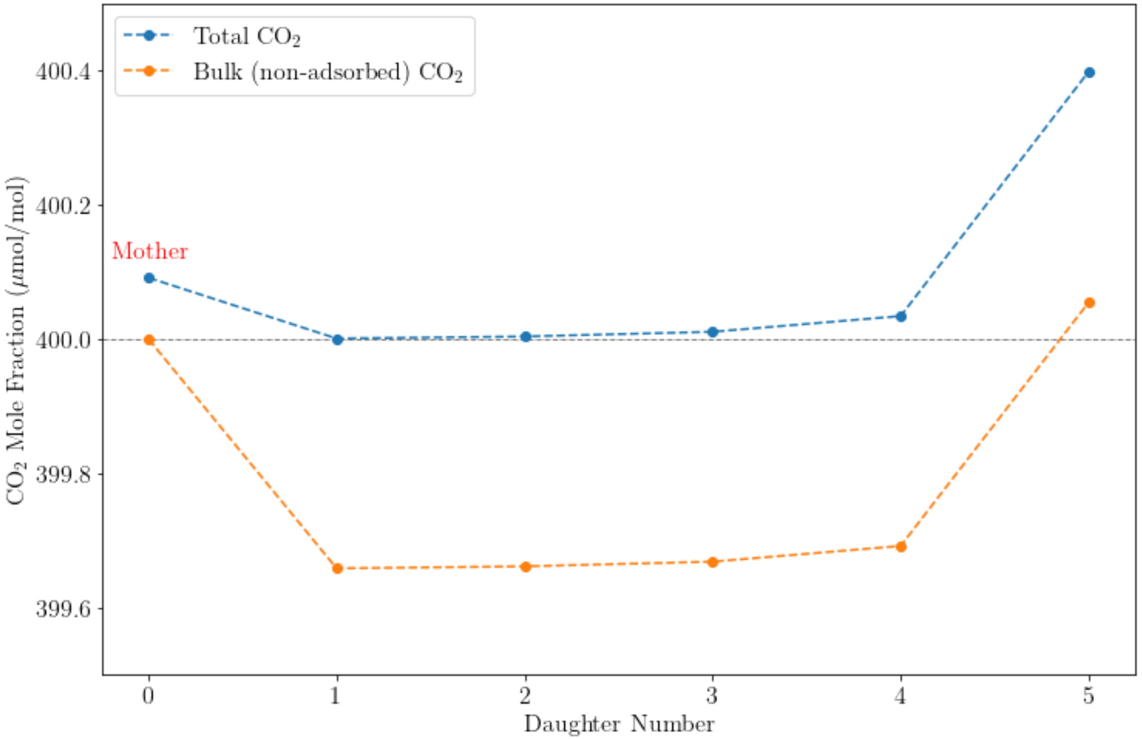
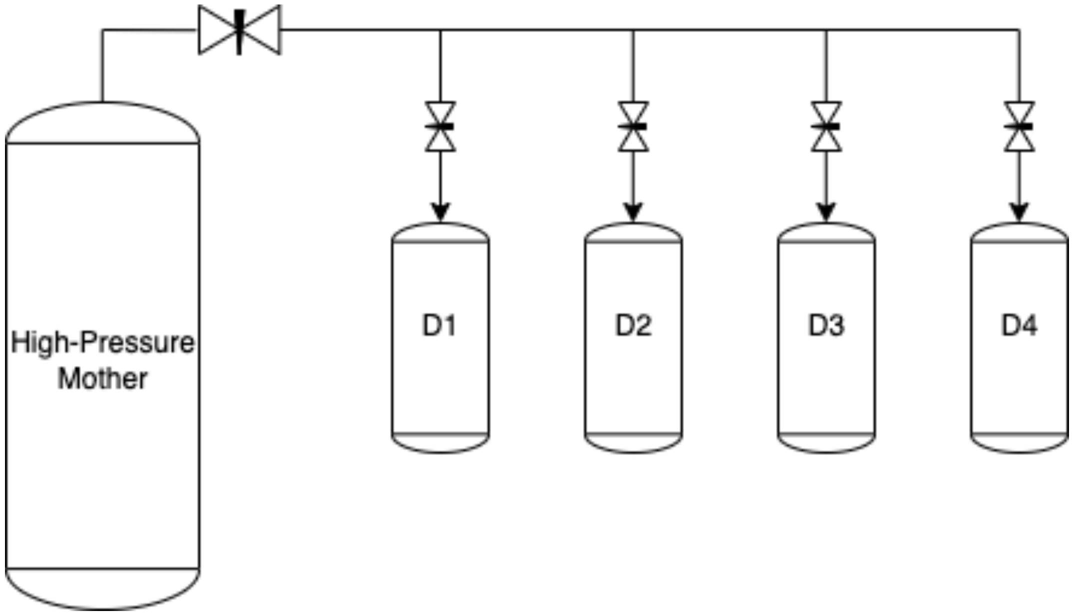
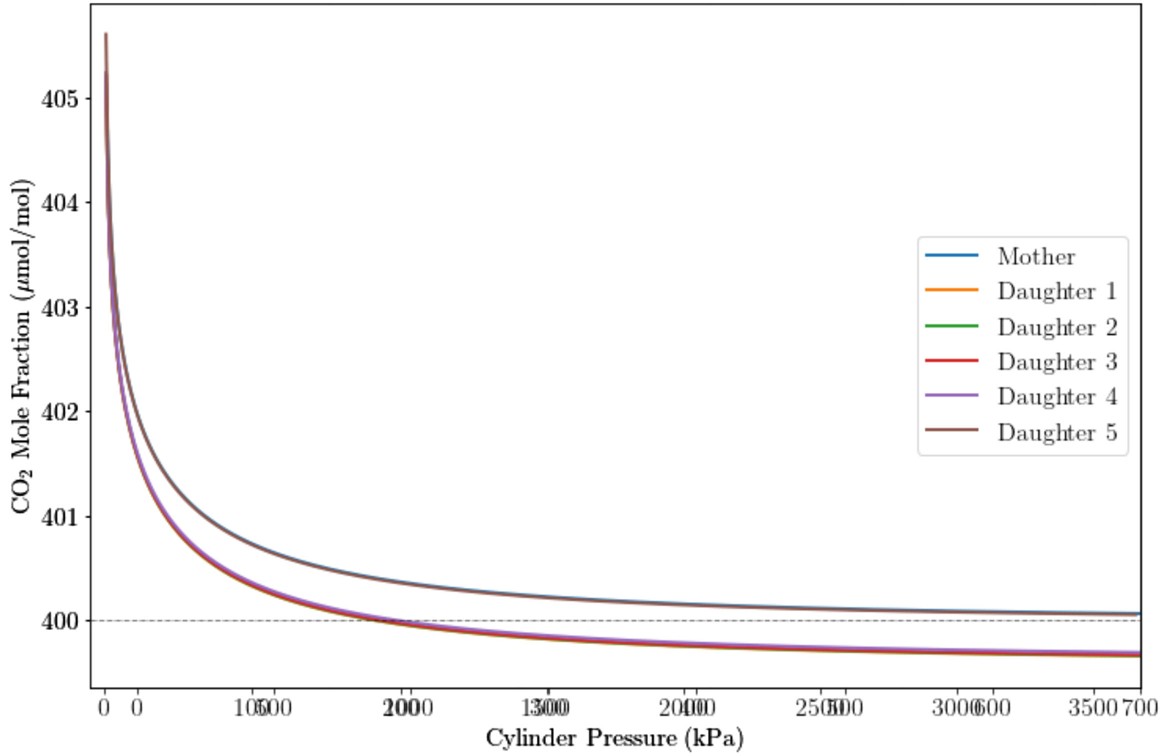




Assumption: daughter vessels have same adsorption characteristics as mother

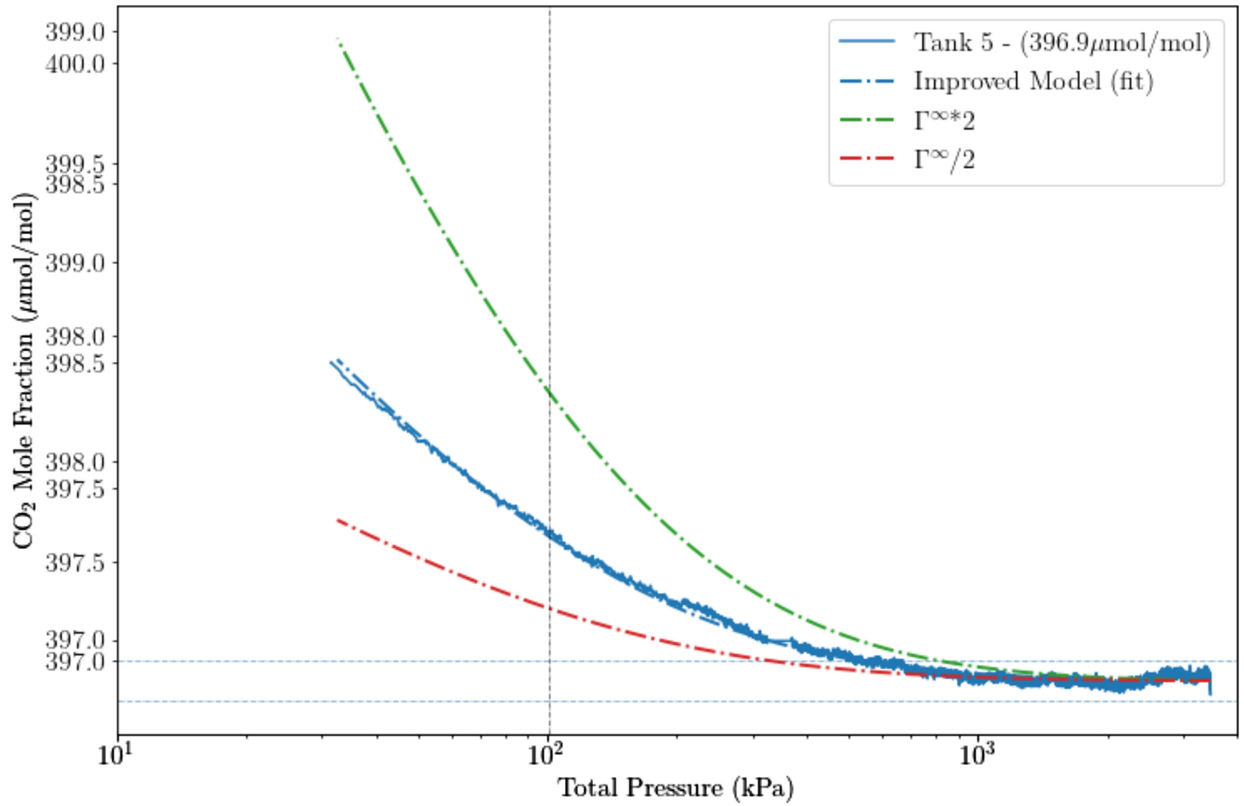
Mother/Daughter Generation Tests





Now decant the daughter vessels

Parameter Sensitivity



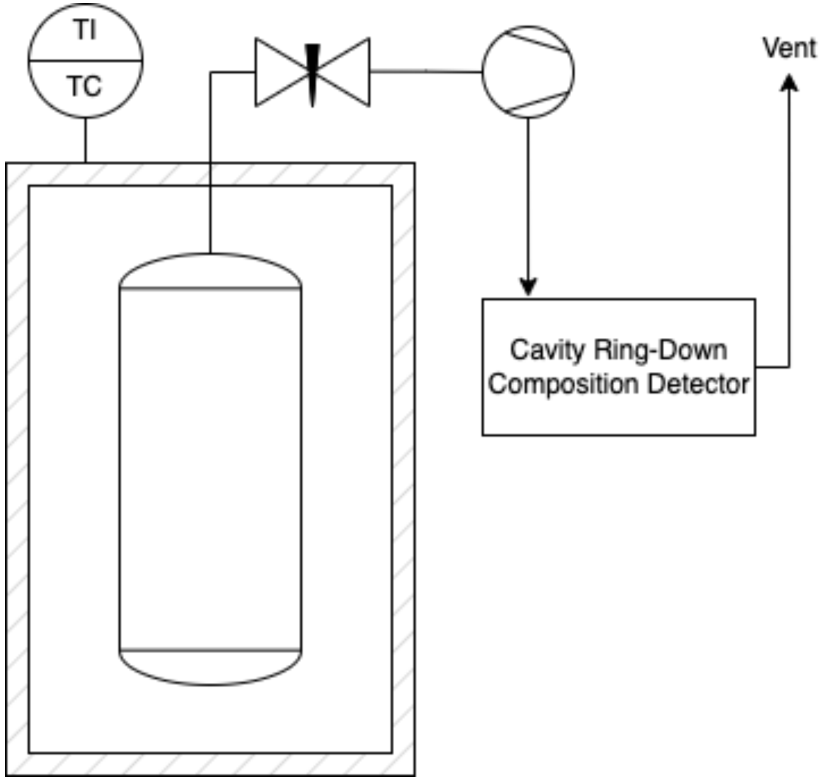
Langmuir Parameters:

$$\Gamma_i = \Gamma^\infty \frac{K_i\, p_i}{1 + K_i\, p_i}$$

K_i: Pressure Scale
Γ^∞: Maximum Adsorption

Expectations:
K_i: Incr (Decr) → Decr (Incr) Desorption p
Γ^∞: Incr (Decr) → Incr (Decr) "Loss"

Multiple Adsorbing Species



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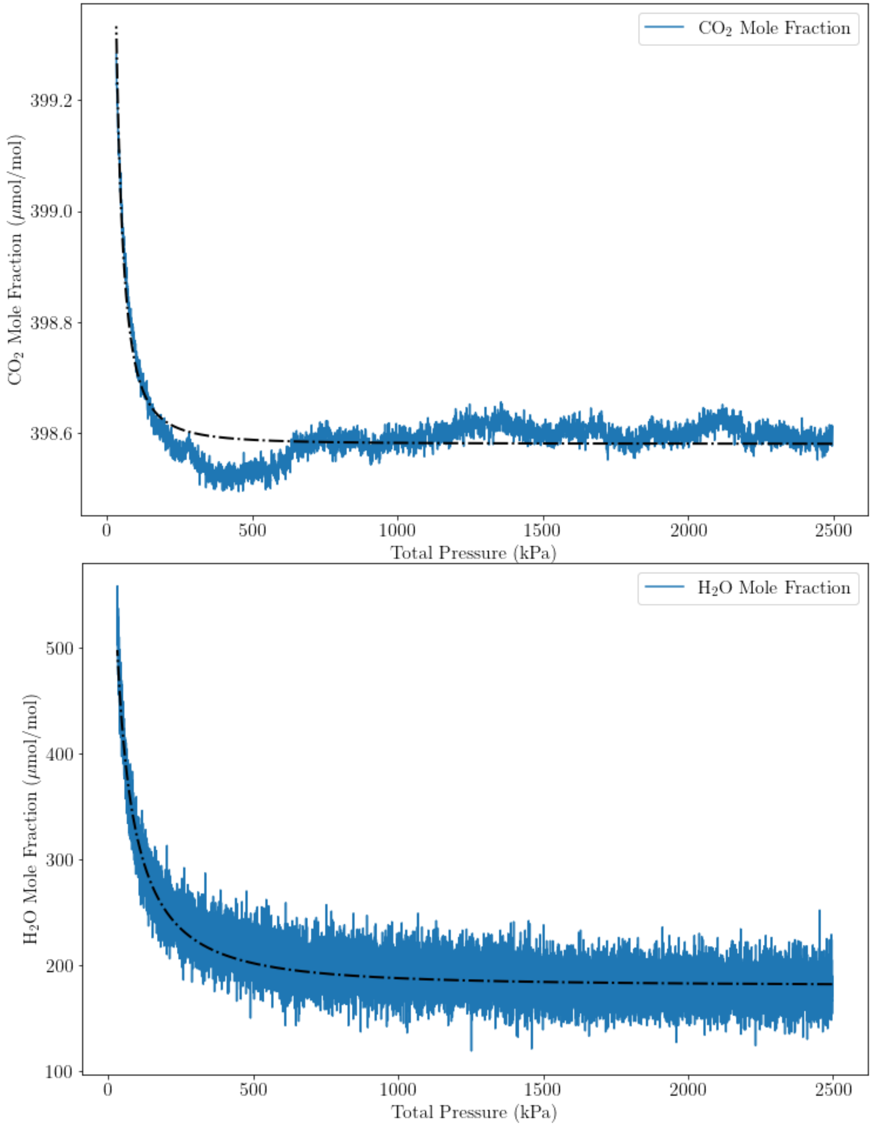
Loss Function	$\frac{dN_i}{dt} = -y_i\dot{N}$ where $y_i = \frac{N_{b,i}}{\sum_m N_{b,m}} = \frac{p_i}{p}$
Adsorption Constraint	Extended Langmuir: $\Gamma_i \cdot \frac{A}{V} = \left(\frac{\Gamma^\infty A}{V}\right)\frac{K_i\,p_i}{1+\sum_j K_j\,p_j}$
Other	Isothermal (no heat/energy balance) Normalize extensive quantities by *V*
Solution Method	Euler integration, stop/start equilibrium [forward propagation, recompute EQ conditions, repeat]

Extended Langmuir: Same adsorption sites / surface area, each adsorbing species has different equilibrium constant

Binary / Competitive Adsorption



- Test example: CO_2 (~400 µmol/mol) *and* H_2O (~200 µmol/mol) in Air
- H_2O mole fraction increases by 250 %
- Extended Langmuir Model fails to fit experimental measurements
- *Test single component model: independent fits to measurements, but is physically inconsistent:* $\Gamma^{\infty}(H_2O) = 500 \times \Gamma^{\infty}(CO_2)$
- Inconclusive modeling; H_2O adsorption mechanism is clearly different from CO_2, but the correct adsorption mechanism (for H_2O and CO_2, and any interaction) is not clear

Conclusions and Future Work

- **New apparatus can mimic use of reference gas vessels; data fit trends that are consistent with Langmuir-type adsorption**
- **Improved model can fit experimental measurements, yielding adsorption fitting parameters that allow for other modeling (M/D transfers), sensitivity testing, and examination of vessels with multiple adsorbing species**
- **Future measurements will focus on gas mixtures that show competitive or co-adsorption, with the intention of fitting the measured composition traces to our improved model**
- **Caveat: More complex adsorption models may be necessary.**