Analysis of “problem” molecules: Ammonia, and Hydrogen Chloride

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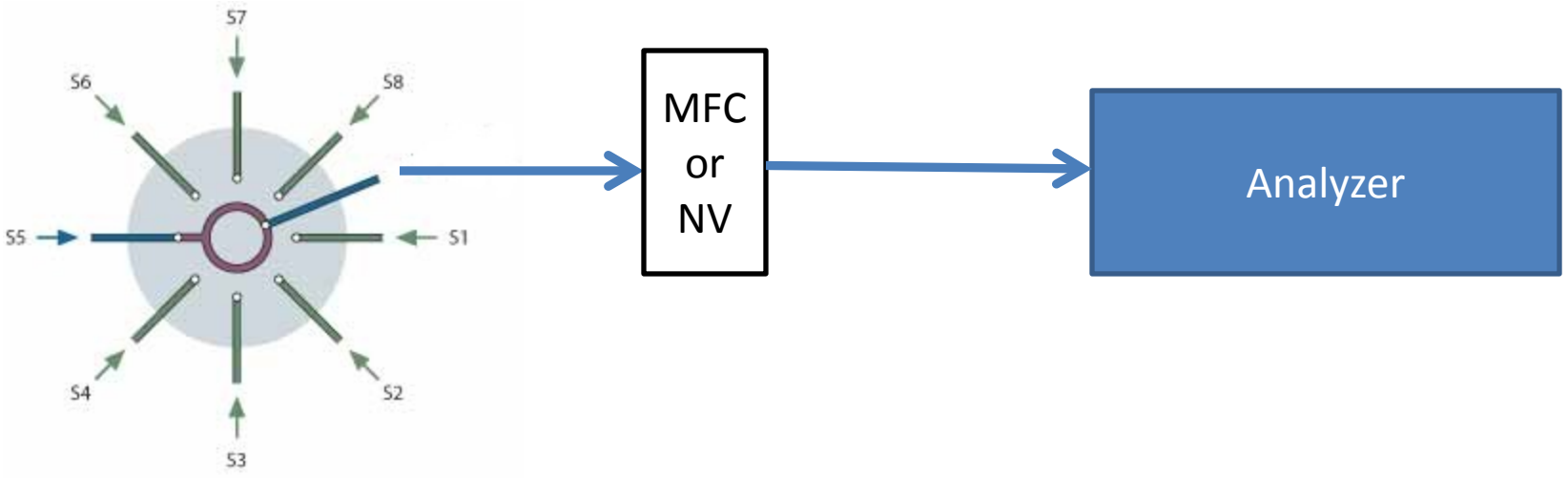
Lisbon, Portugal

Outline

- Gas Auto Sampling - Standard Format
- Gas Auto Sampling - Refined Format
- Results - Ammonia
- Results - Hydrogen Chloride
- Gas Auto Sampling - Major Change

Computer Operated Gas Auto Sampler (COGAS)
Standard Format



<u>Hardware:</u>

PSMs Available

Gas Regulator - 30 psig

PFA Tubing

Other Samples Dead Ended

<u>Acquisition:</u>

2 Samples per Control

Up to 6 Minute Purge

Up to 2 Minute Data Averaging

<u>Components:</u>

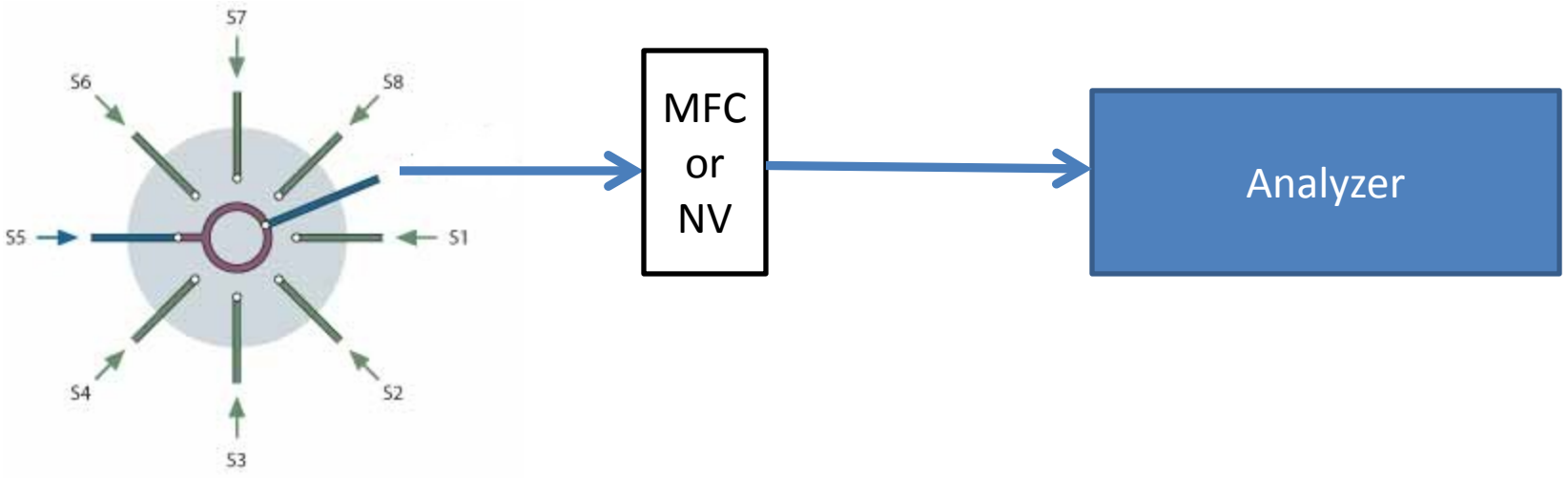
CO_2; CO;

CH_4; C_3H_8; O_2

SO_2; NO; NO_2; H_2S

Precision ≤ 0.2% Rel.

Computer Operated Gas Auto Sampler (COGAS)
Small Refinement



<u>Hardware:</u>

PSMs Available

Gas Regulator - 30 psig

SS Tubing – Silconert 2000 coated

Other Samples Dead Ended

<u>Acquisition:</u>

1 Sample per Control

Up to **10** Minute Purge

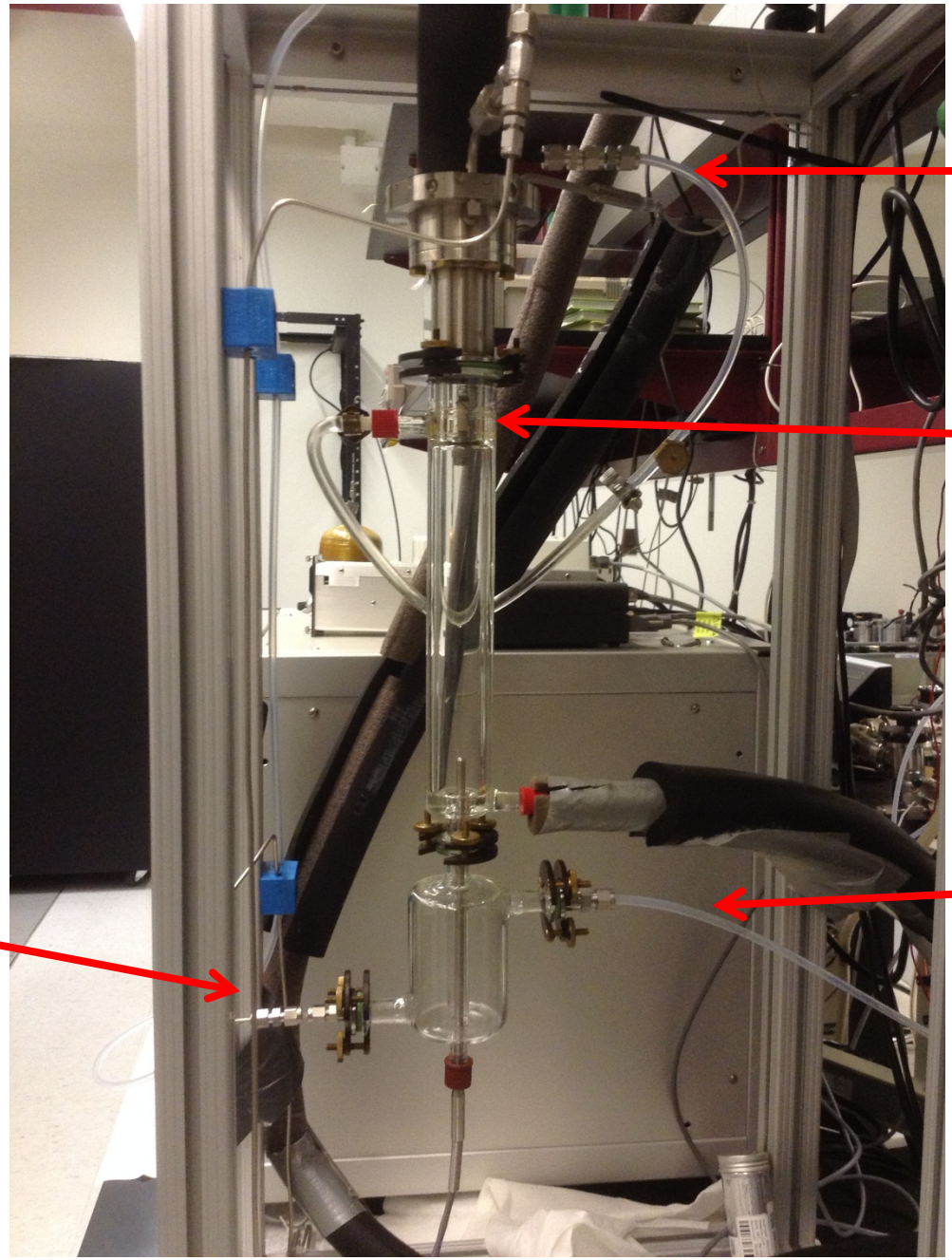
Up to 2 Minute Data Averaging

Permeation Tube Vs. Compressed Gas Cylinder

Production of Gas Mixture Standard:

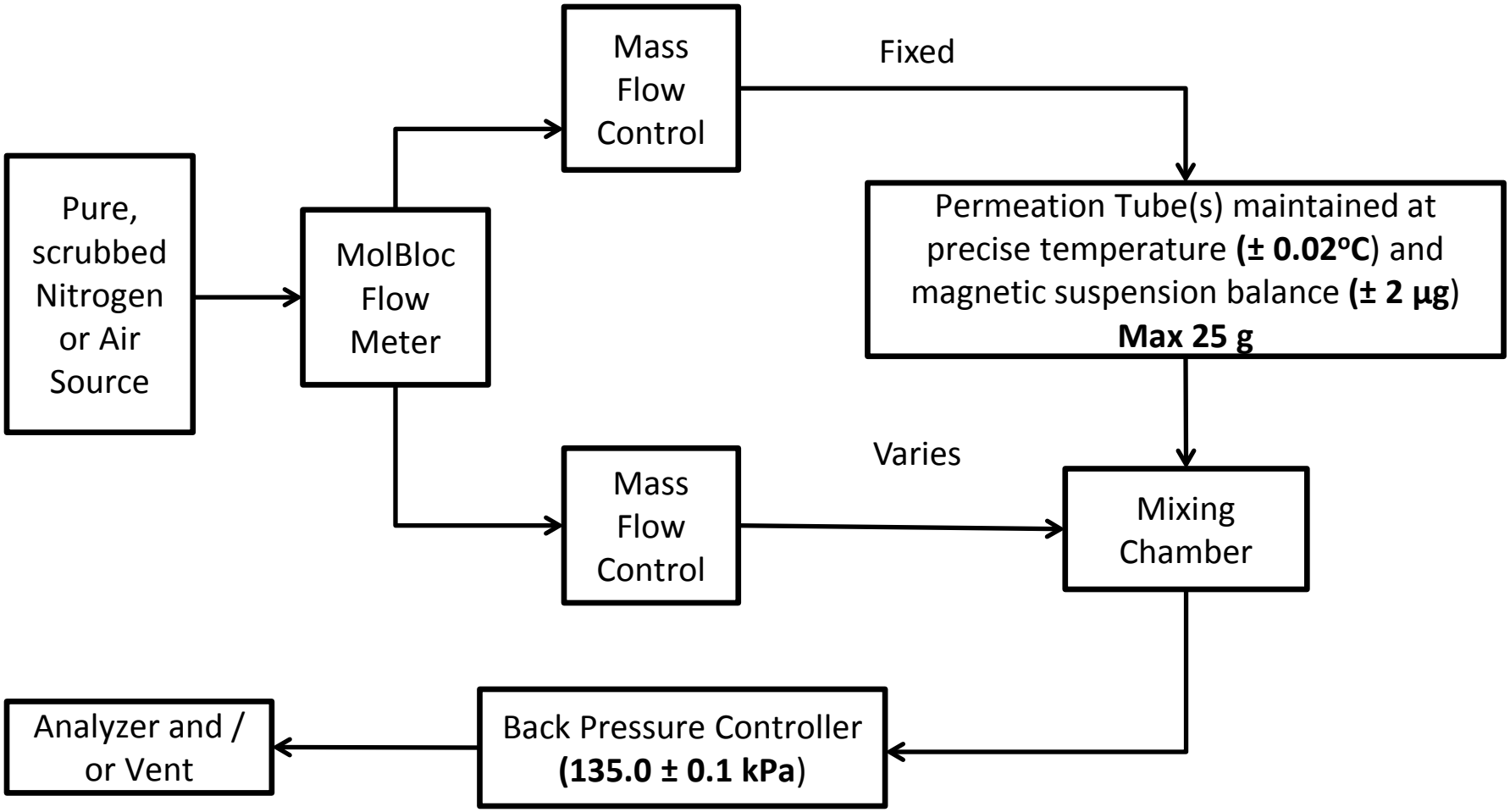
- Single Component (≤ 50 µmol/mol)
- Nitrogen or Air Balance

Category	Permeation Tube	Compressed Gas Cylinder
Standard Type	**Dynamic**	**Static**
Standard is Portable	**No**	**Yes**
Number of Dilution Steps	**1**	**≥ 4**
Possible Immediate Loss to Walls	**N/A**	**Yes**
Possible Unstable Gas Mixture	**N/A**	**Yes**
Direct Handling of Hazardous Material	**No**	**Yes**

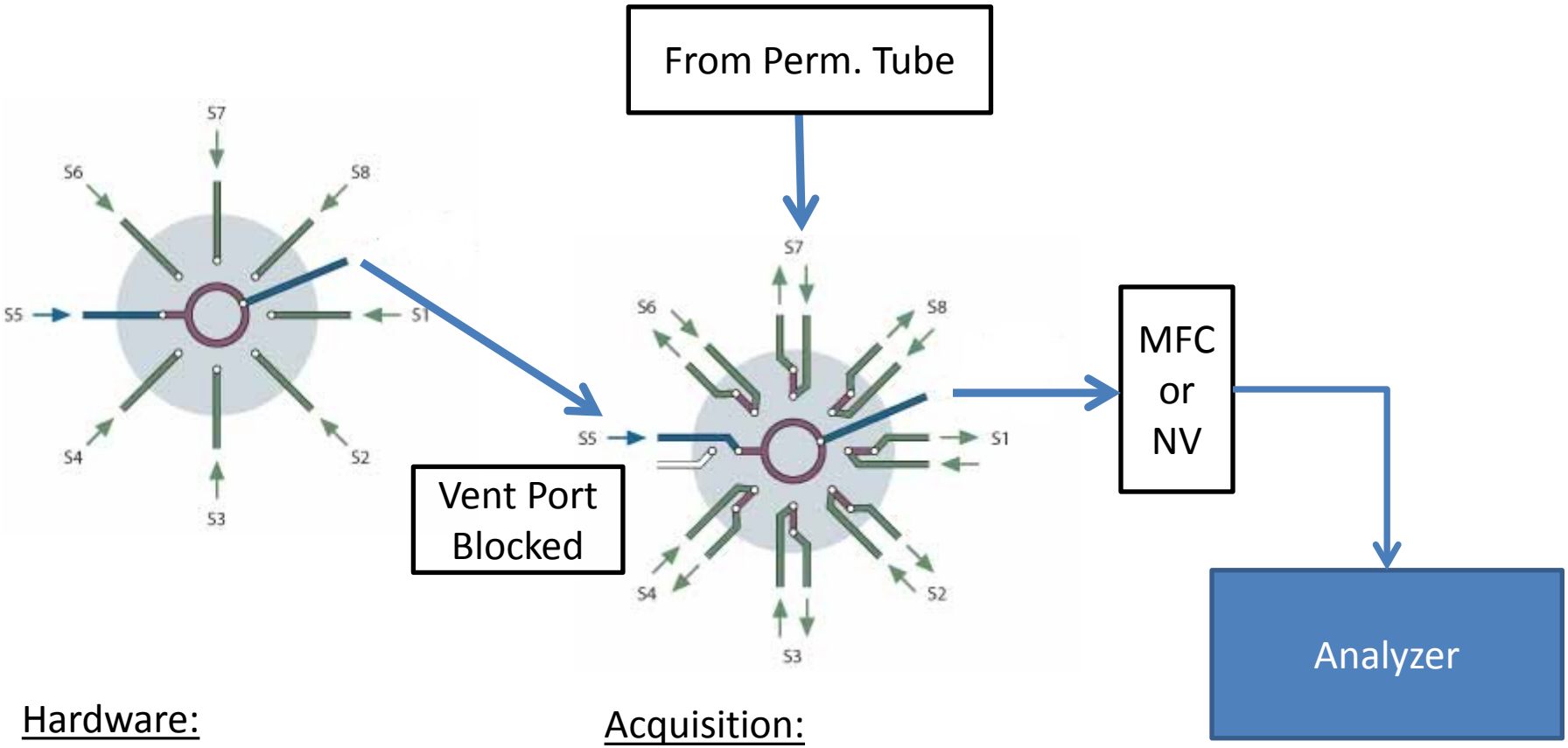

Fixed Gas Flow
Perm. Tube
Vary Gas Flow
Outlet

Permeation Device System

Continuous-weighing mode compliant with ISO 6145 Part 10



Computer Operated Gas Auto Sampler (COGAS)
Refined Format



Hardware:

Gas Regulator - 30 psig

No PSMs Available

Other Samples Dead Ended

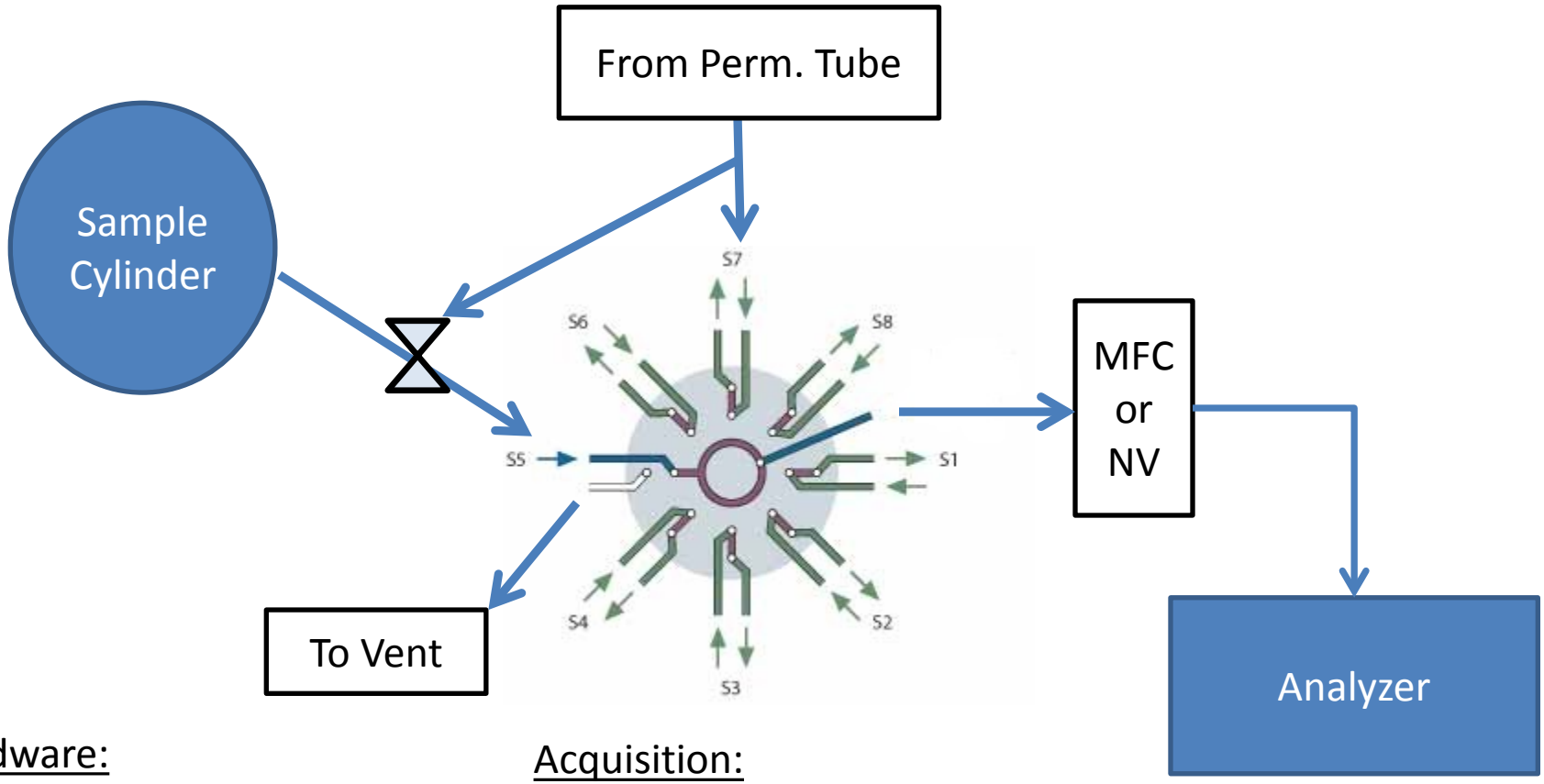
Acquisition:

1 Sample per Control

Up to 10 Minute Purge

Up to 2 Minute Data Averaging

Computer Operated Gas Auto Sampler (COGAS)
Further Refined Format



Hardware:

Gas Regulator - 30 psig

No PSMs Available

Switching Valve

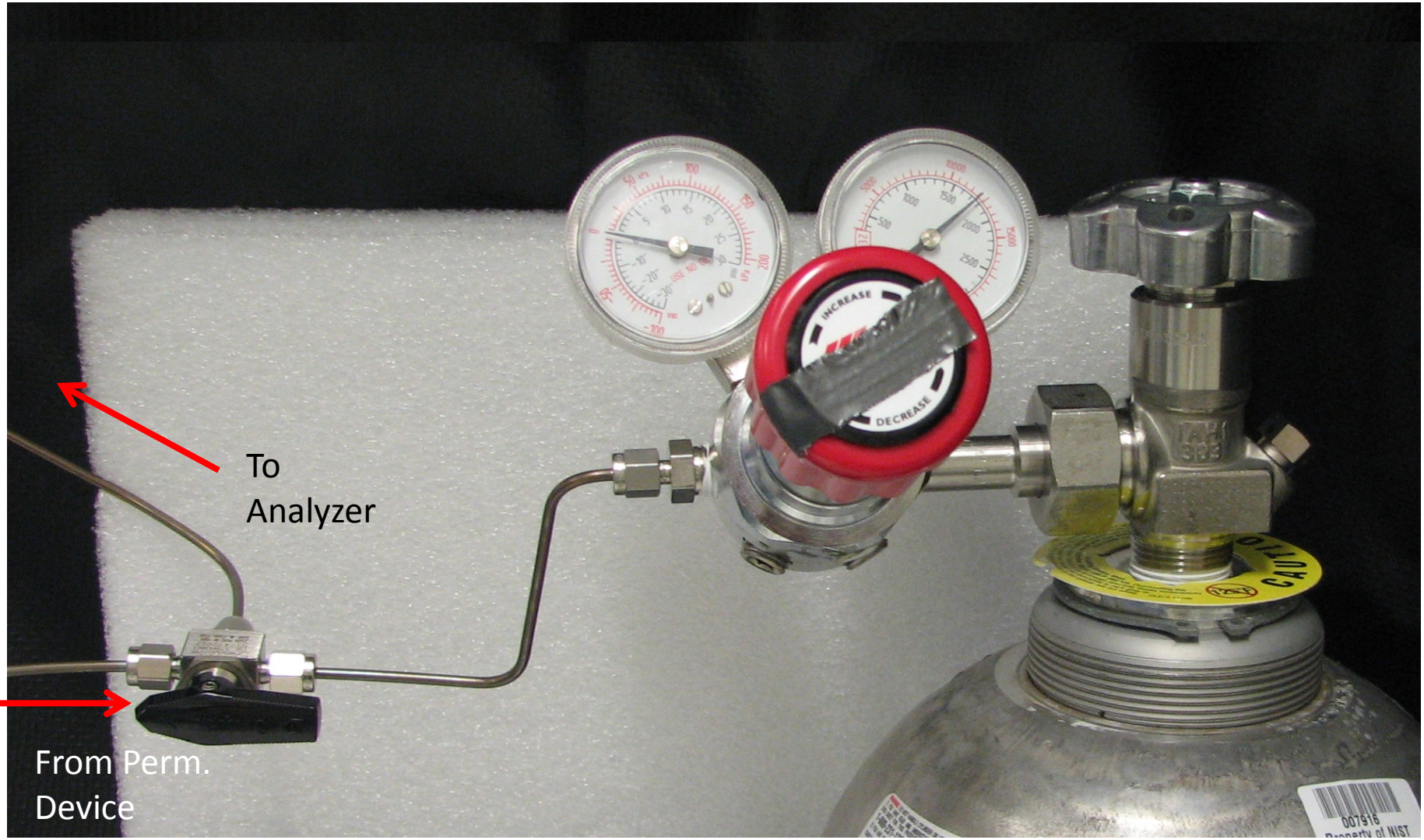
Acquisition:

Sample used as Control

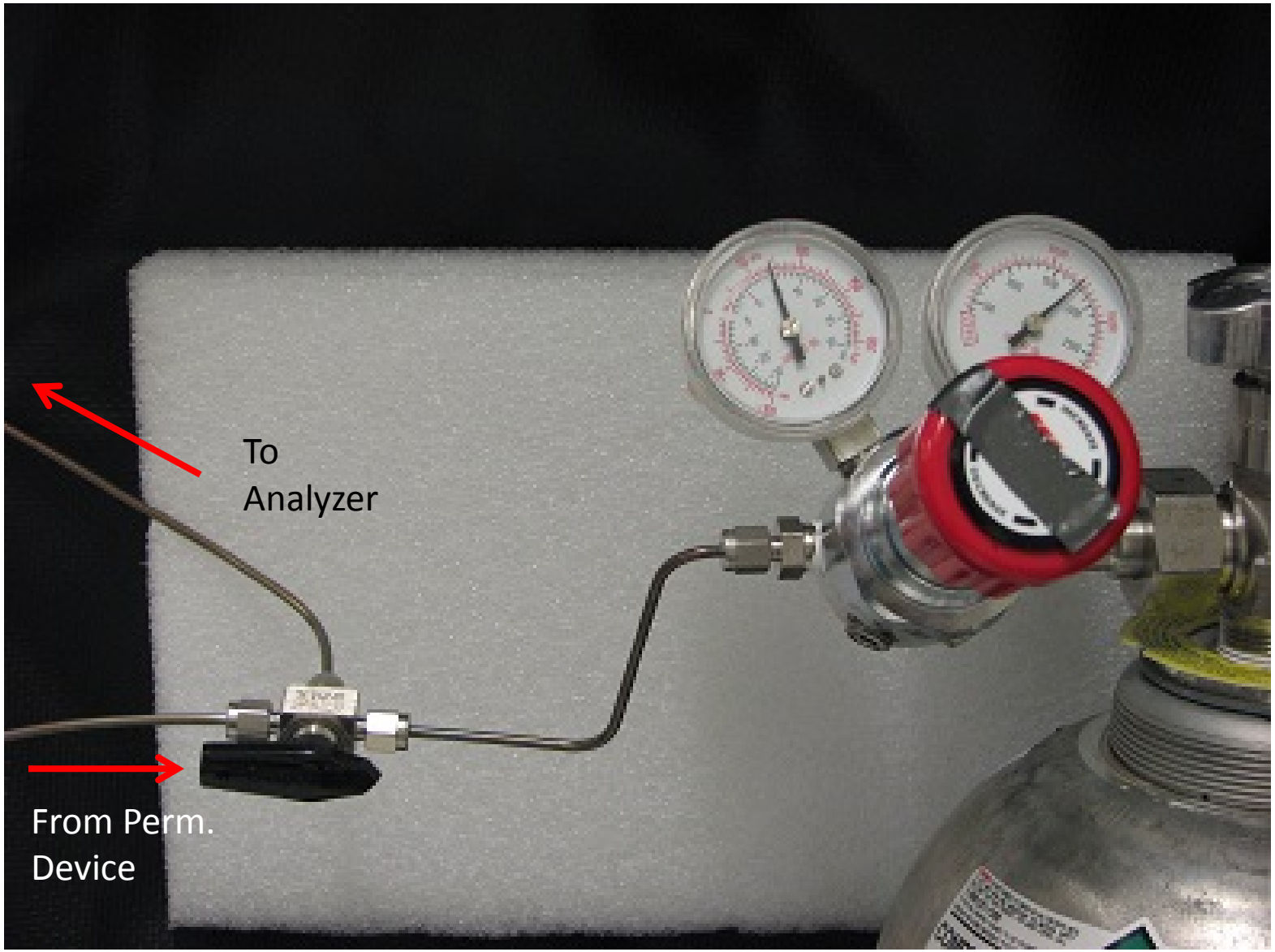
Up to 10 Minute Purge

Up to 2 Minute Data Averaging

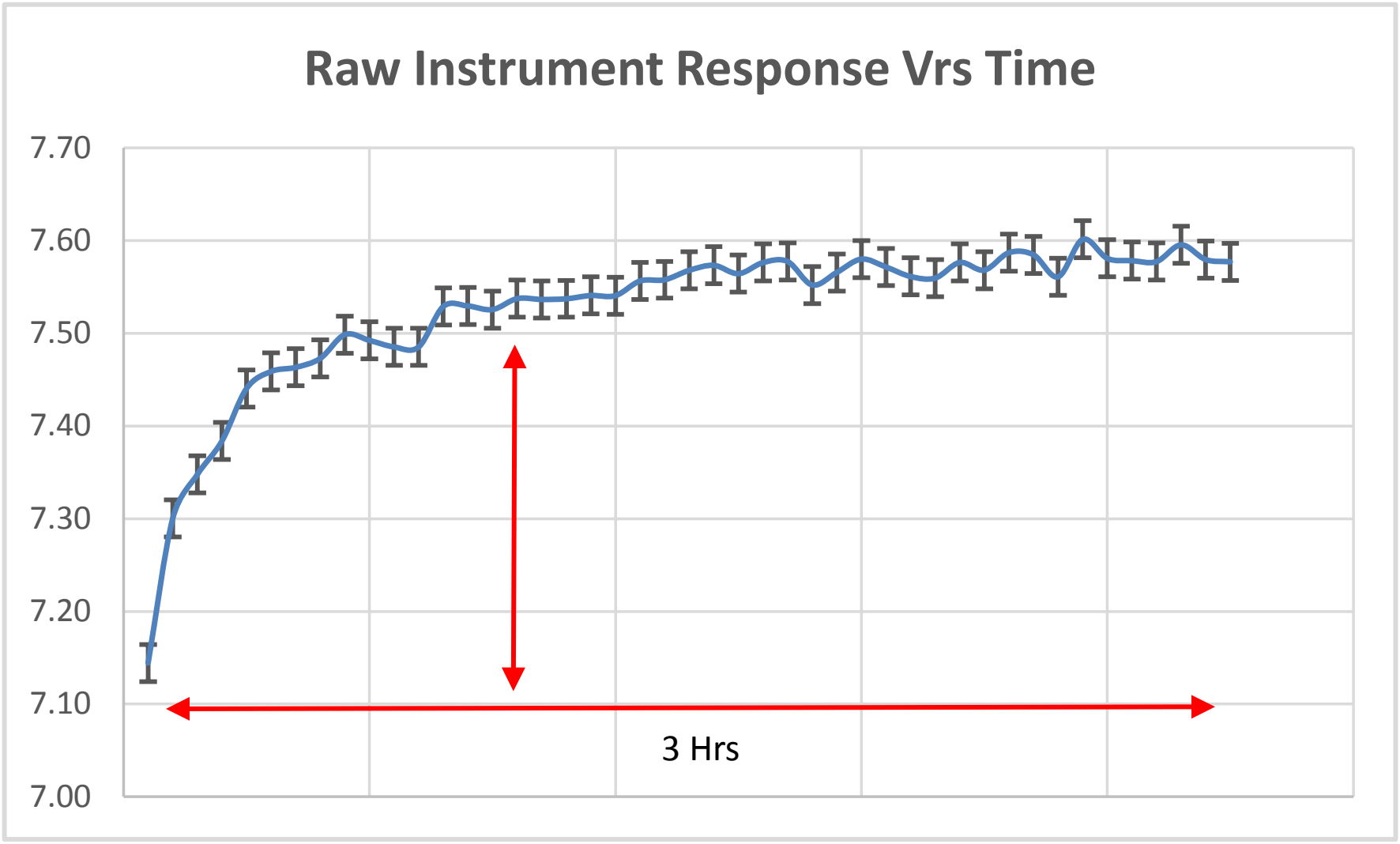
NH_3 Analysis - Preparation

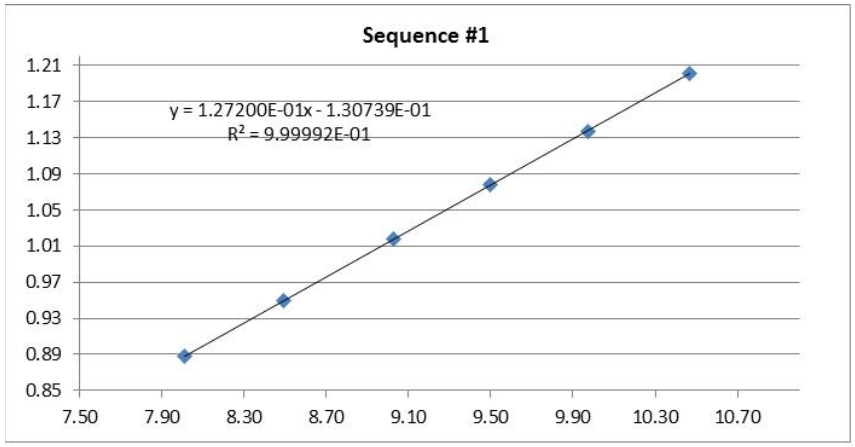


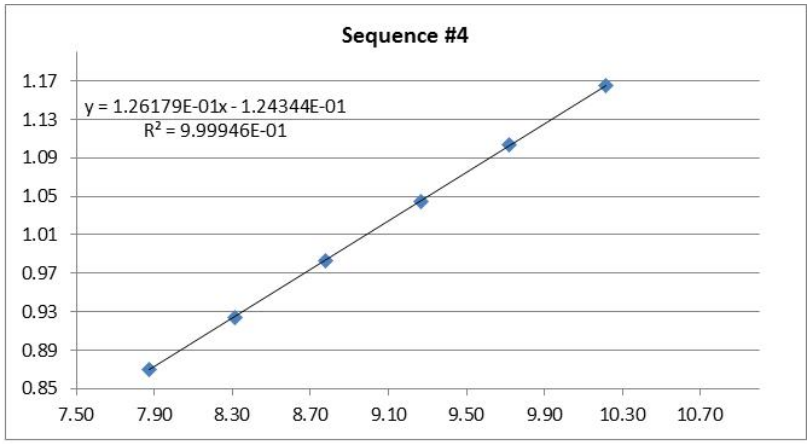
NH_3 Analysis - Preparation



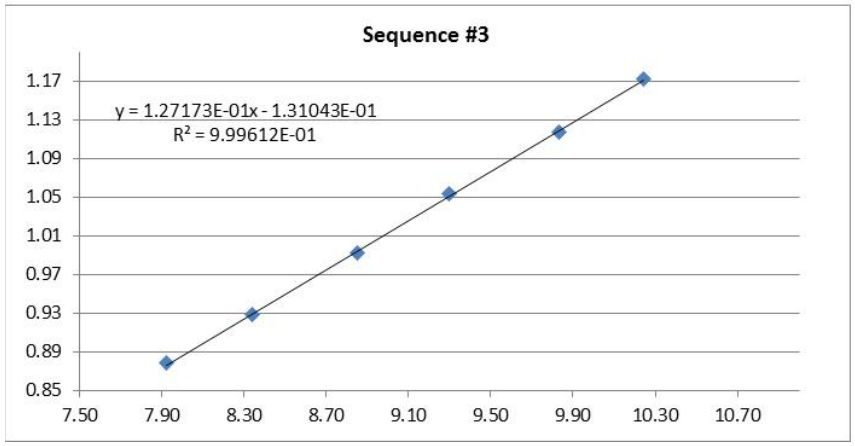
9 Nominal µmol/mol NH_3 Response by Chemilumenesence

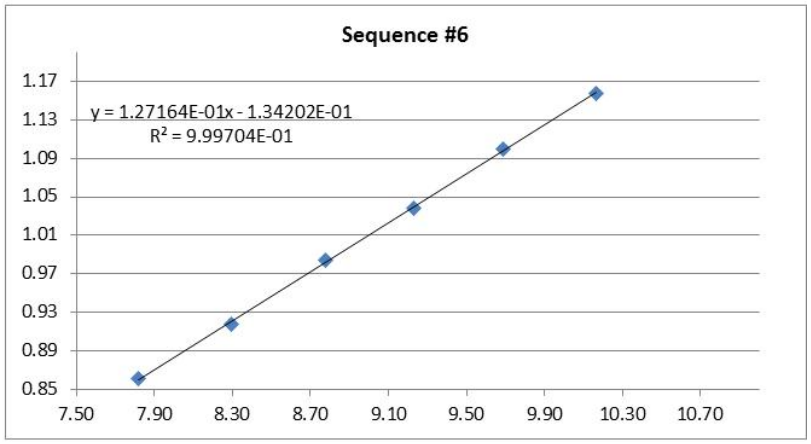






	Seq#: 1	Seq#: 2	Seq#: 3	Seq#: 4	Seq#: 5	Seq#: 6
m:	1.27200E-01	1.28054E-01	1.27173E-01	1.26179E-01	1.27238E-01	1.27238E-01
c:	-1.30739E-01	-1.39998E-01	-1.31043E-01	-1.24344E-01	-1.34317E-01	-1.34317E-01
Control (ppm):	**8.889**	**8.902**	**8.894**	**8.911**	**8.915**	**8.915**
Previous (ppm):	8.88	8.88	8.88	8.88	8.88	8.88
%Diff:	0.11	0.25	0.15	0.35	0.39	0.39





Cylinder Number	2011 Analysis NH_3 (µmol/mol)	2013 Analysis NH_3 (µmol/mol)	%Difference
KAL002649	27.74 ± 0.34	27.67 ± 0.28	-0.25
KAL002651	29.44 ± 0.36	29.41 ± 0.29	-0.09
AAL071147	9.51 ± 0.12	9.62 ± 0.10	1.15
AAL071153	9.38 ± 0.12	9.38 ± 0.10	-0.01
AAL071013	9.50 ± 0.12	9.51 ± 0.10	0.10
AAL071027	9.25 ± 0.11	9.37 ± 0.10	1.30
AAL072344	8.88 ± 0.11	8.89 ± 0.10	0.11

No Flow of Sample when Perm Tube is Analyzed

Continuous Sample Flow

NH_3 Certification - Current Capabilities and Methodology

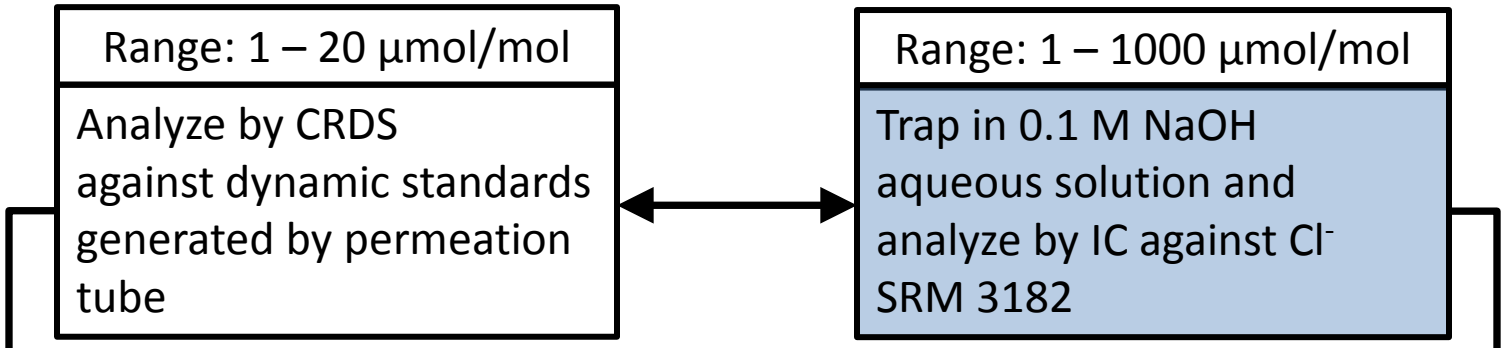
- Certify from 5 to 50 µmol/mol at **1%** Expanded Uncertainty
- Condition Analyzer using Perm Tube Process Flow
- Confirm Equivalence of Perm Tube Process Flow through COGAS and directly to Analyzer
- Sample used as Control
- Initial **One** Hour Sample Purge, 5 minutes thereafter
- Sample flow at 300 cc/min to Analyzer
- Sample flow at 100 cc/min to Vent, while Analyzing Perm Tube Flow to Analyzer

Original Roadmap of Certification of HCl

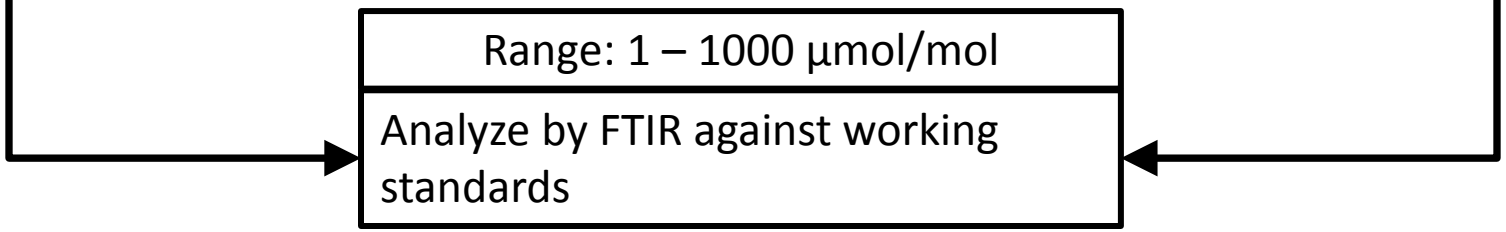
Objective: Expanded Uncertainty of ≤ 1% Relative

Range: 1 to 1000 µmol/mol HCl in Balance N_2

Certify Working Standards



Certify Customer Samples



HCl - Preparation

Wash with 1 M HCl

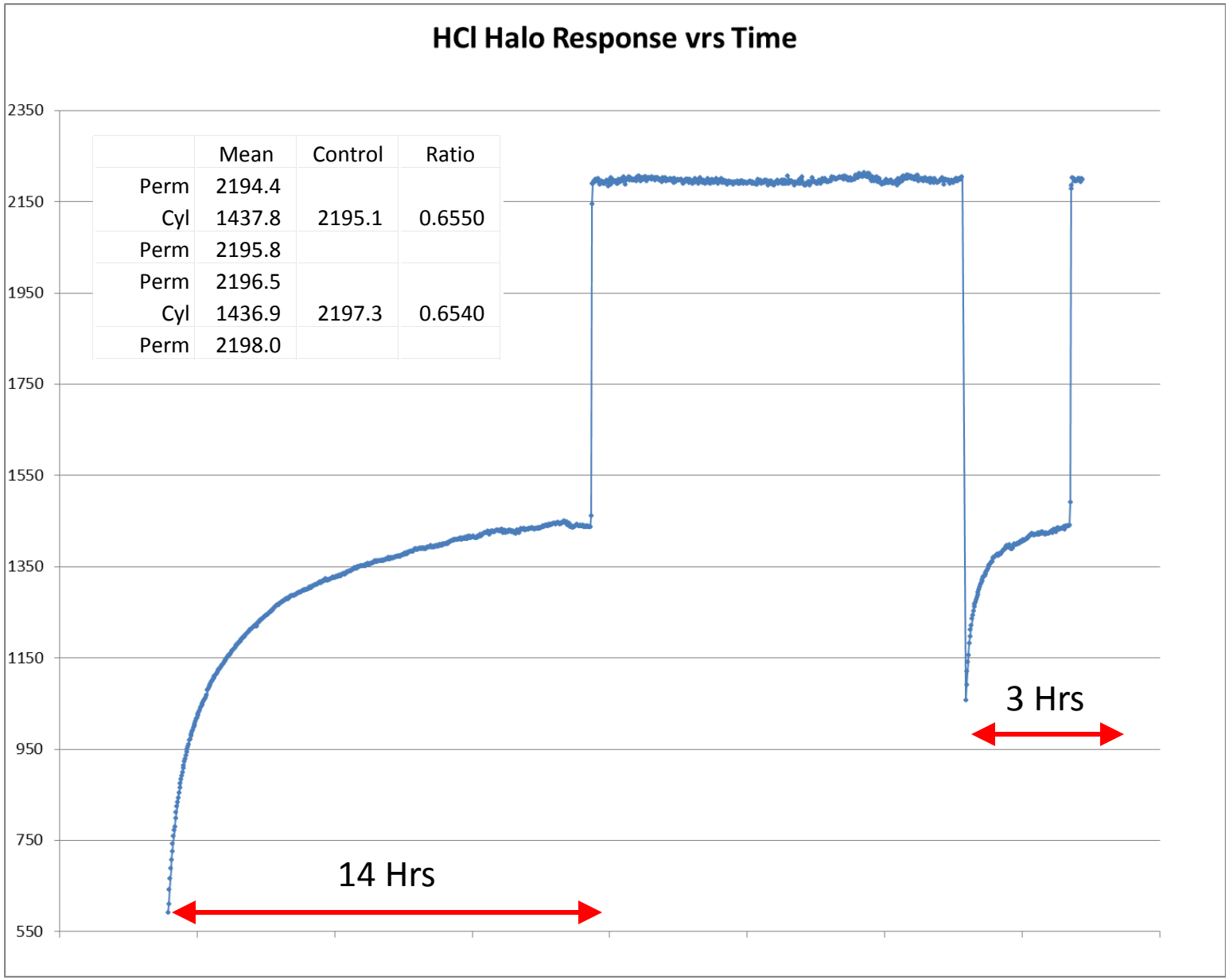
Wash with Water

Wash with Acetone

Dry with N_2

SCOTT
INCREASE
DECREASE
OPEN
CLOSE
PURGE

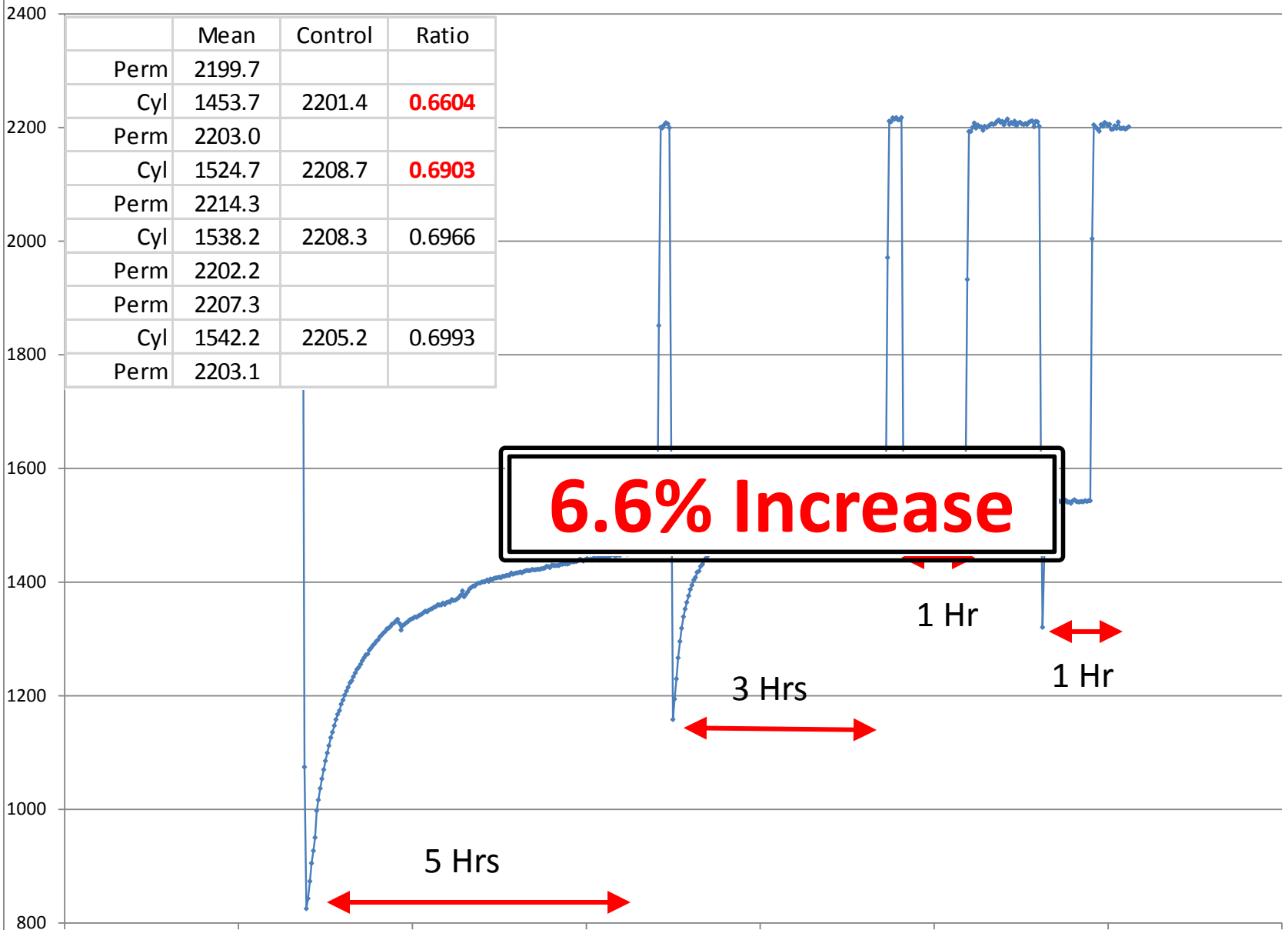
1.8 Nominal µmol/mol HCl Response by CRDS




INCREASE
ROBERTS
OXYGEN
DECREASE
COMPRESSED
GAS. N.O.S.

HCl Halo Response vrs Time

	Mean	Control	Ratio
Perm	2199.7		
Cyl	1453.7	2201.4	**0.6604**
Perm	2203.0		
Cyl	1524.7	2208.7	**0.6903**
Perm	2214.3		
Cyl	1538.2	2208.3	0.6966
Perm	2202.2		
Perm	2207.3		
Cyl	1542.2	2205.2	0.6993
Perm	2203.1		



Low HCl Certification - Current Capabilities and Methodology

- Certify from 1 to **5** µmol/mol at **2**% Expanded Uncertainty
- Condition Analyzer using Perm Tube Process Flow
- Confirm Equivalence of Perm Tube Process Flow through COGAS and directly to Analyzer
- Sample used as Control
- Initial **Eight** Hour Sample Purge, 10 minutes thereafter
- Sample flow at 300 cc/min to Analyzer
- Sample flow at 100 cc/min to Vent, while Analyzing Perm Tube Flow to Analyzer

Low HCl Certification - Next Steps

Reduce the EIGHT hour Purge Time !!

Replace Two Stage Regulator with:

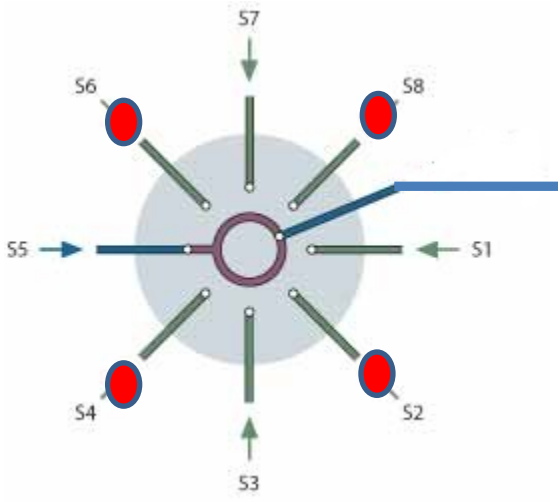
- Silconert 2000 Coated, Low Volume, Single Stage Regulator
- Restriction Valve – gas must ALWAYS be flowing

Coatings:

- Sample Selection Valve
- Use the highly Hydrophobic Dursan coating

Develop a High Pressure COGAS with One Regulator

High Pressure COGAS - Purging Mode



High Pressure: 2000 psig

Low Pressure: 30 psig

Regulator

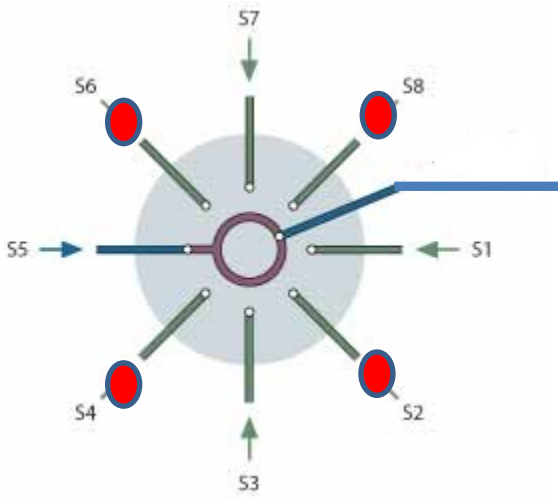
MFC

To Vent

House N_2

Analyzer

High Pressure COGAS - Analyzing Mode



High Pressure: 2000 psig

Low Pressure: 30 psig

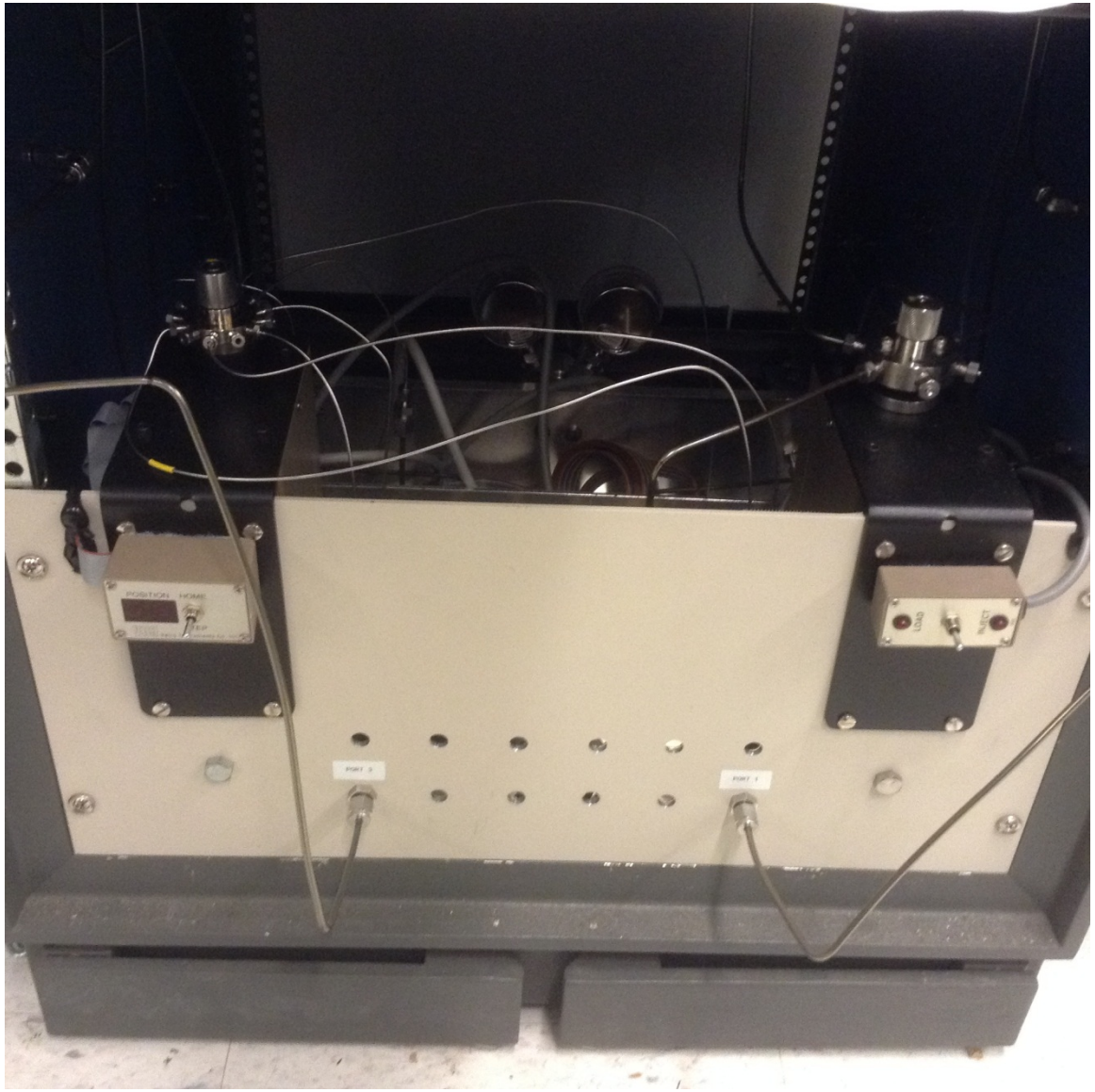
Regulator

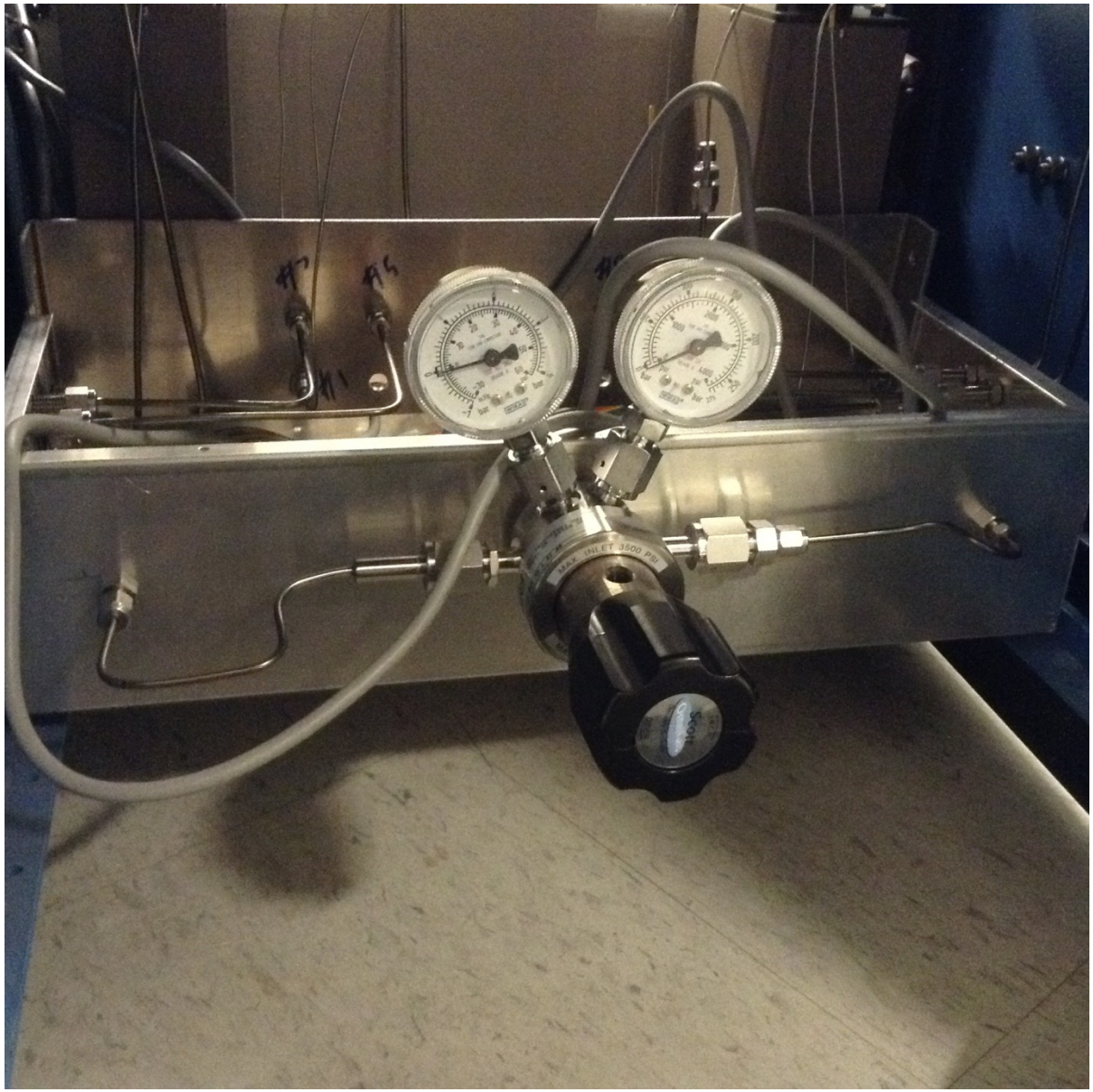
MFC

To Vent

House N_2

Analyzer


POSITION
HOME
PORT 2
PORT 1


MAX. INLET 3500 PSI

Questions ?