Material and Process Conditions for Successful Use of Extractive Sampling Techniques

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Acknowledgement

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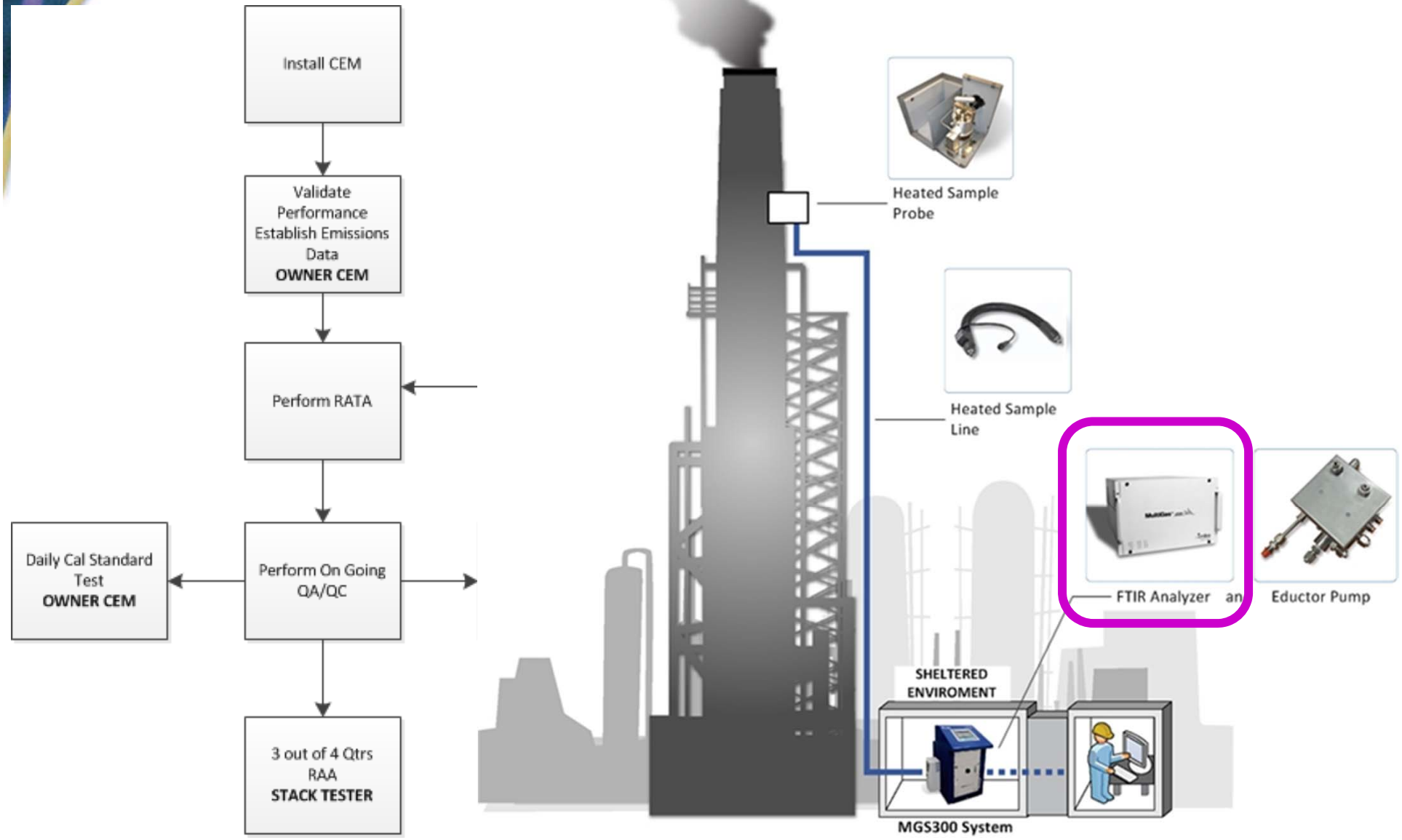
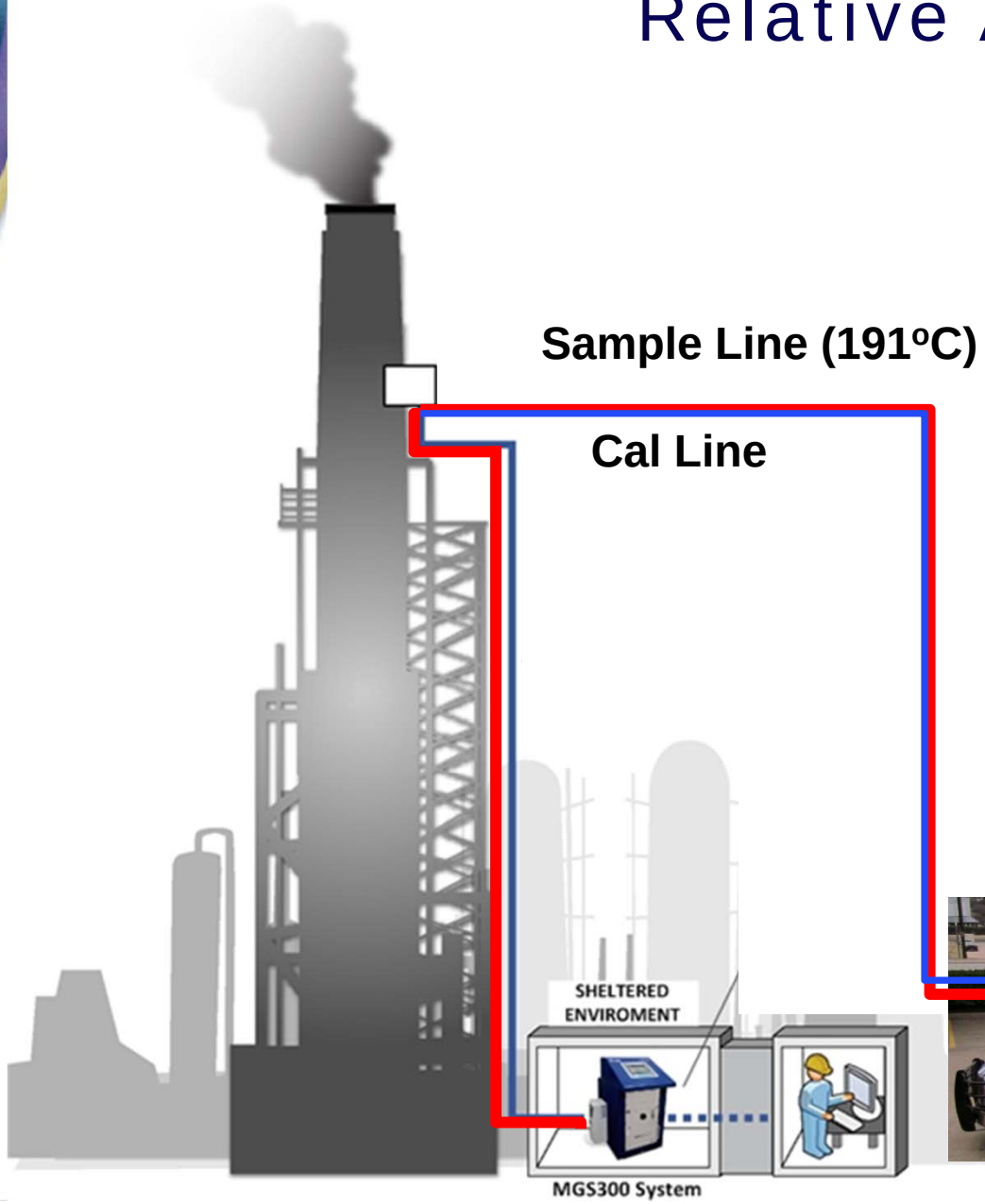
  - Principal Applications Engineer at MKS Instruments, Inc.
  - In the Process & Environmental Analysis Solutions group

Continuous Emissions Monitoring US EPA Clean Air Act

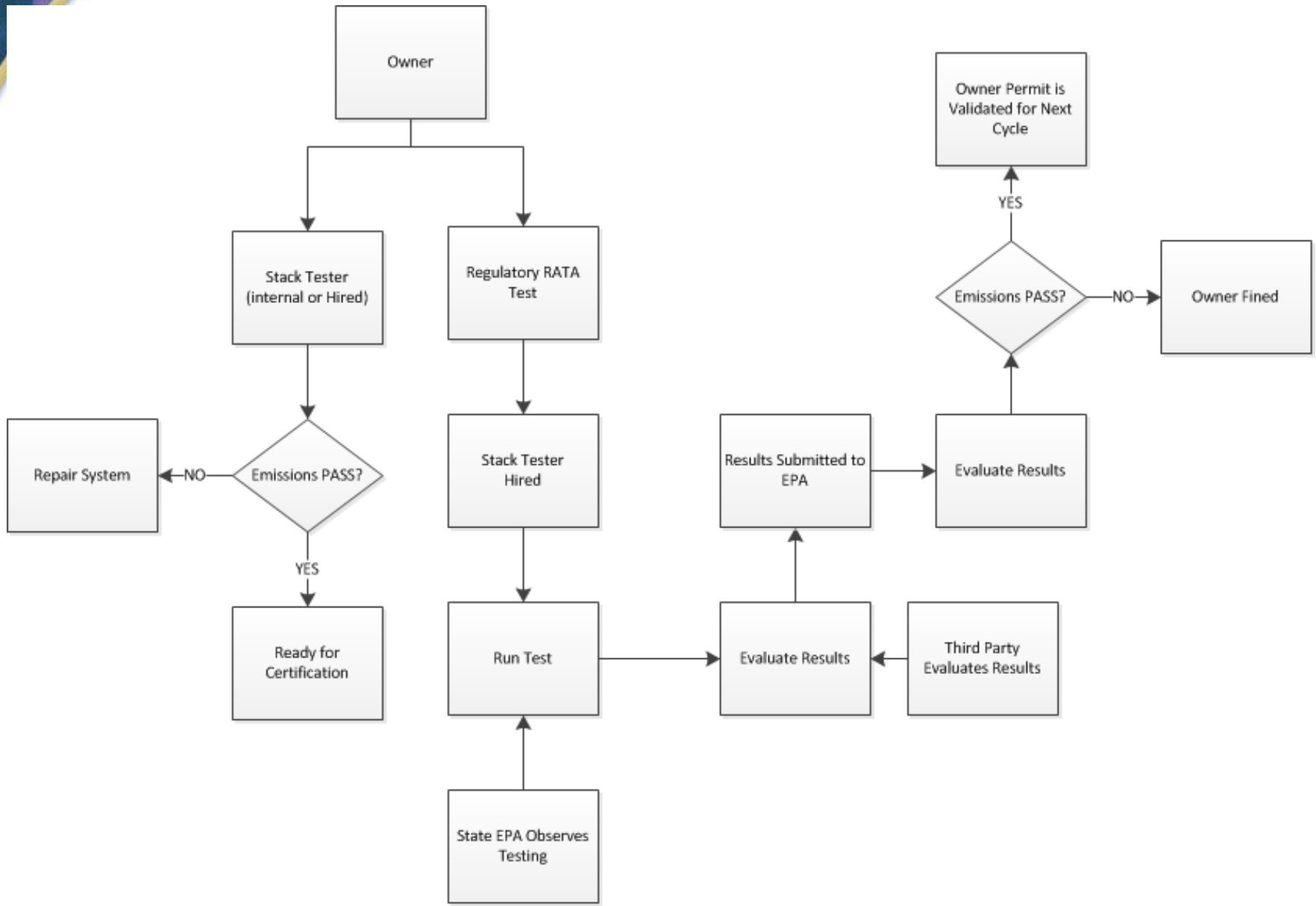


Certifying Emissions Compliance
Relative Accuracy Test Audit



3rd Party Stack Tester

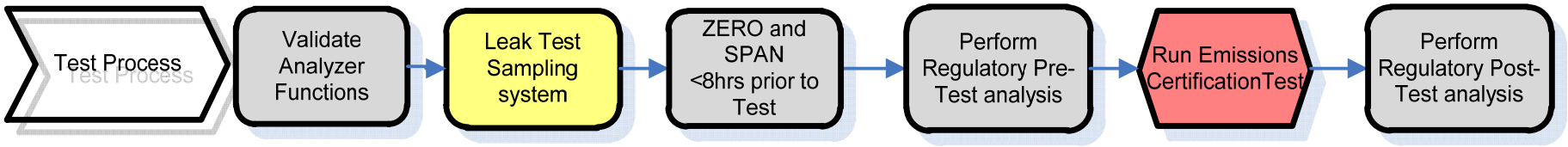
Emissions Testing Process



Emissions Monitoring and Ratification by Extractive FTIR

- Continuous Emissions Monitoring (CEM)
  - Continuous deployment in climate controlled hut or enclosure
  - Stack Emissions compliance recorded regularly following Governing body regulations (EPA, EU)
  - Cement kiln, Power plants, Incinerators
- Emissions Ratification (Stack Testing)
  - Transport equipment to site for Validation Test
  - Certifying emissions compliance
    - Demonstrate compliance based on site-specific air permit
    - Monthly, quarterly, biannually or yearly basis as listed on permit

Some Good Engineering Practices for On Site Certification Testing

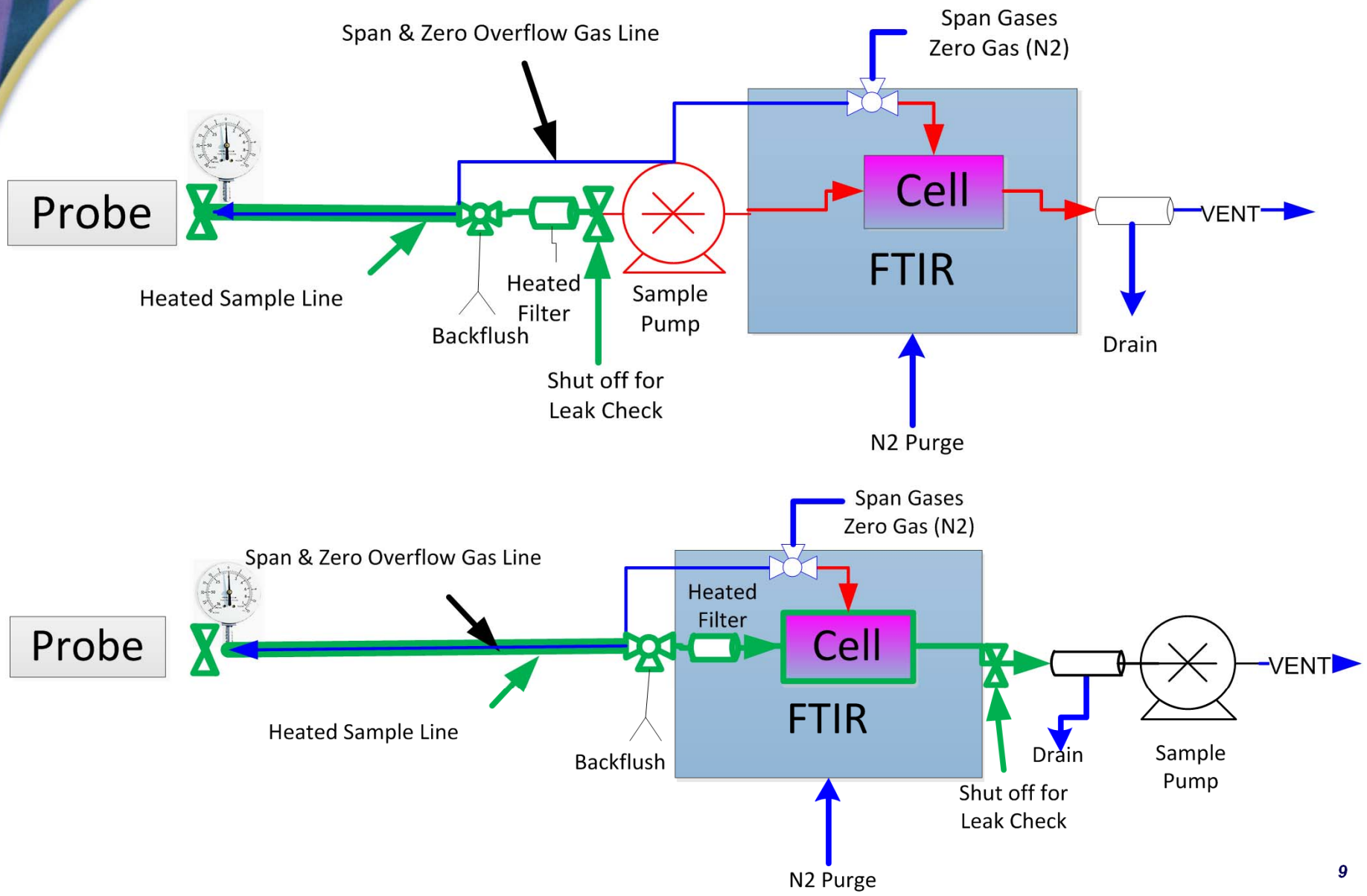


- Validate that the Analyzer is functioning properly
  - Follow Manufacturer's requirements
- Validate that the Sampling system is working properly
  - Make sure the wetted components are clean with no particulates
  - Perform a system Leak Test
  - Perform a system response test (spike recovery or other test)
- Run the analysis
  - Zero and Span the analyzer
  - Perform pre-tests as required by regulatory agency
  - Run the Certification Test
  - Perform pre-tests as required by regulatory agency

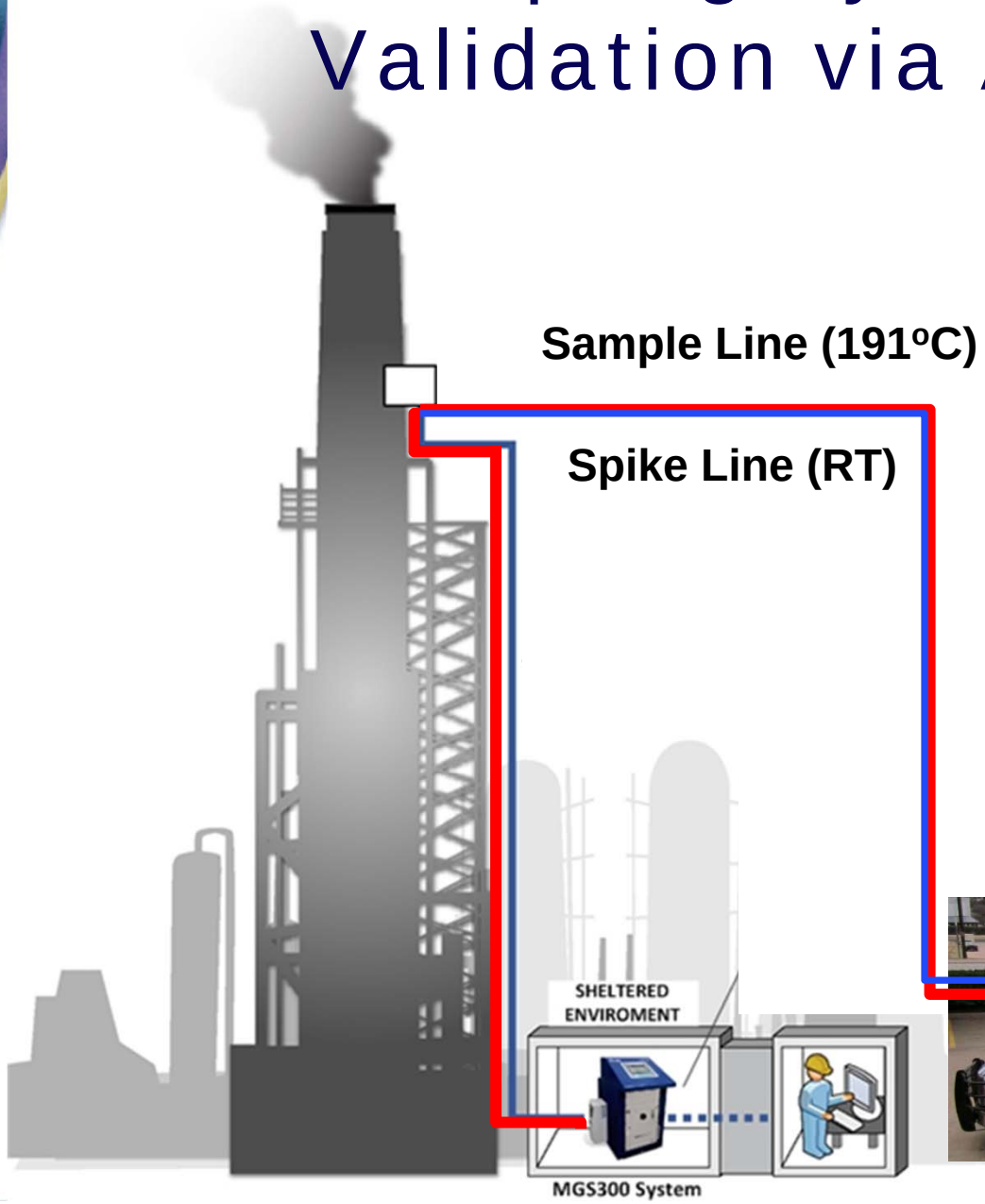
Sampling System Issues that Produce Errors in Analysis

- ANY analyzer using extractive techniques experience these issues!!!
- Sample gas recoveries are not within specification
  - Sampling system has a leak – all gases report low
  - Sample gas flow rate may be too low
- Retention or Condensing of analyte components
  - Gaseous compounds may adhere to sample line, regulator, filter, etc.
    - Proper material selection is needed
  - Gaseous Analytes can condense out of the vapor phase
    - Cold spots in sample line or components
    - Moisture in regulators and on lines
  - Chiller will drop out polar analytes

Sampling System Leak Test



Sampling System and Analyte Validation via Analyte Spiking



- Reference Spike gas replaces 10% of sample gas
- Compare Native concentration, added spike gas concentration to Analyzer value to get % Recovery

3rd Party Stack Tester

Retention or Condensing of Analyte Components

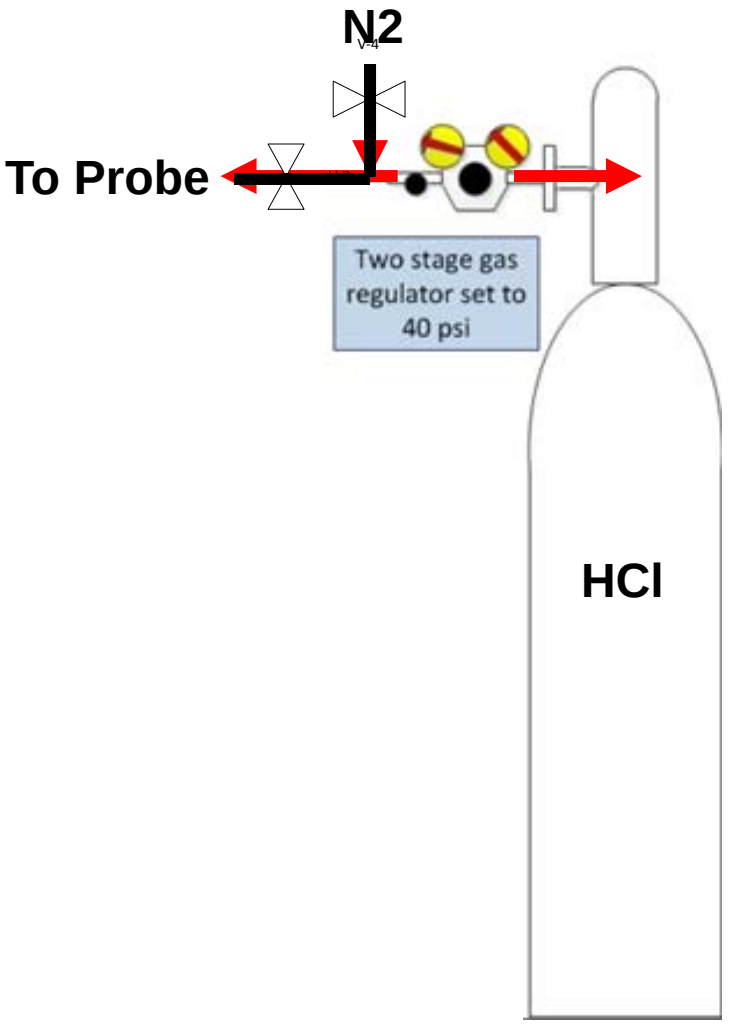
- Reactive Gases
  - React with other gaseous species
  - React/adsorb with wetted materials
  - Water soluble
  - Examples: HCl, NH_3, NO_2, Formaldehyde, HF
- Excessive response times
  - Failure to achieve acceptable t95 times
  - Inability to achieve the certified gas concentration
    - Failed concentration tests
    - Failed spike tests

Sampling System Considerations

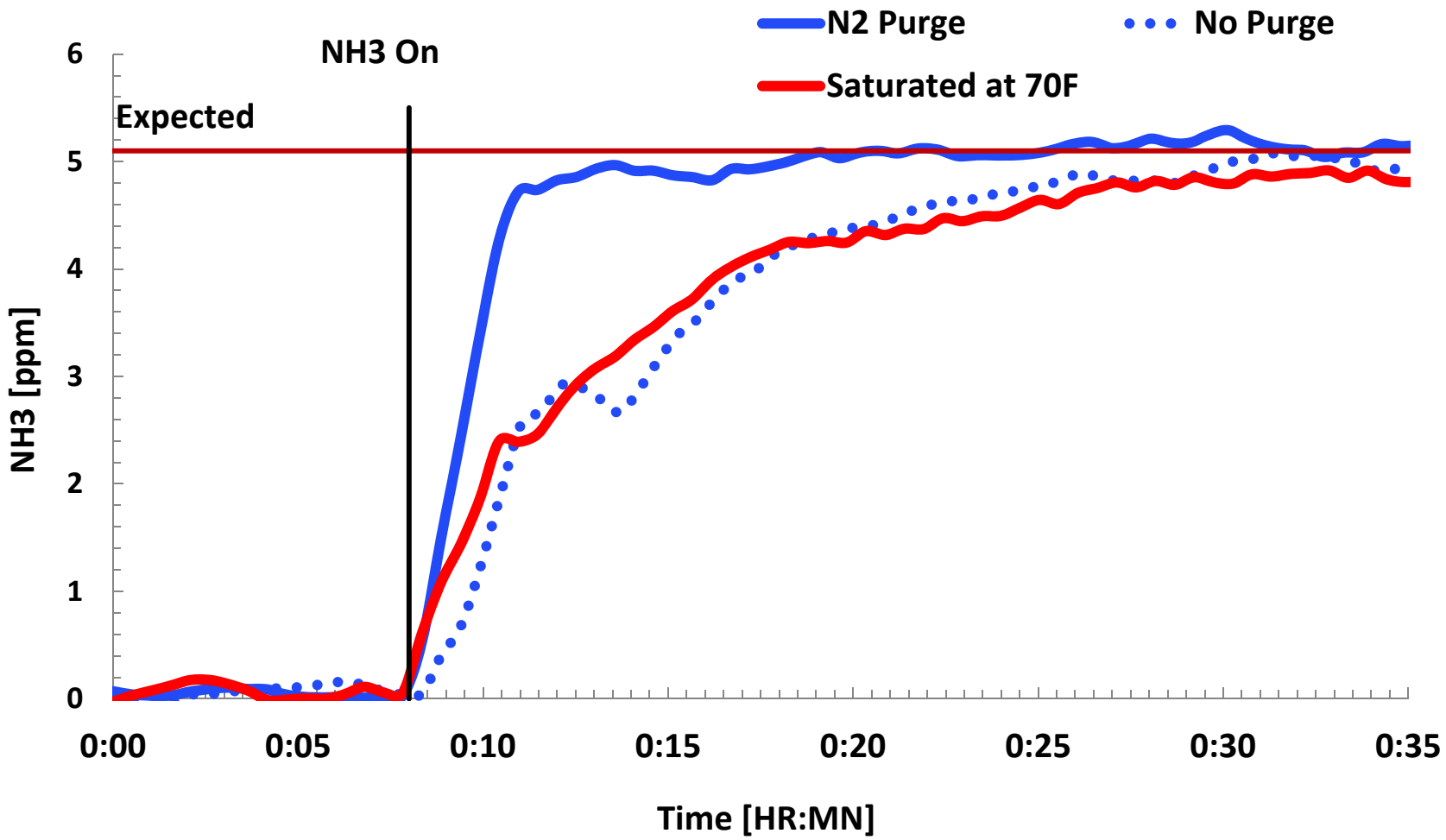
- Wetted Components
  - Calibration Gas Cylinder Pressure Regulator
  - Sample gas probe, heated sampling line, unheated calibration gas line
  - Analyzer internal wetted surfaces – FTIR gas cell
- Sampling System Temperatures
  - Typical extractive sample line temperatures 191 °C
  - Some emissions tests allow lower temperatures ~120 °C
- Typical Wetted Line Materials
  - HDPE – High-density polyethylene (max temp 110 °C)
  - PTFE – Polytetrafluoroethylene (max temp 260 °C)
  - PFA – Perfluoroalkoxy (max temp 260 °C)
  - Stainless Steel coated with SilcoNert® or uncoated
- Gas flow rate
  - Higher flow rates preferred (3 to 7 LPM)

Pressure Regulator

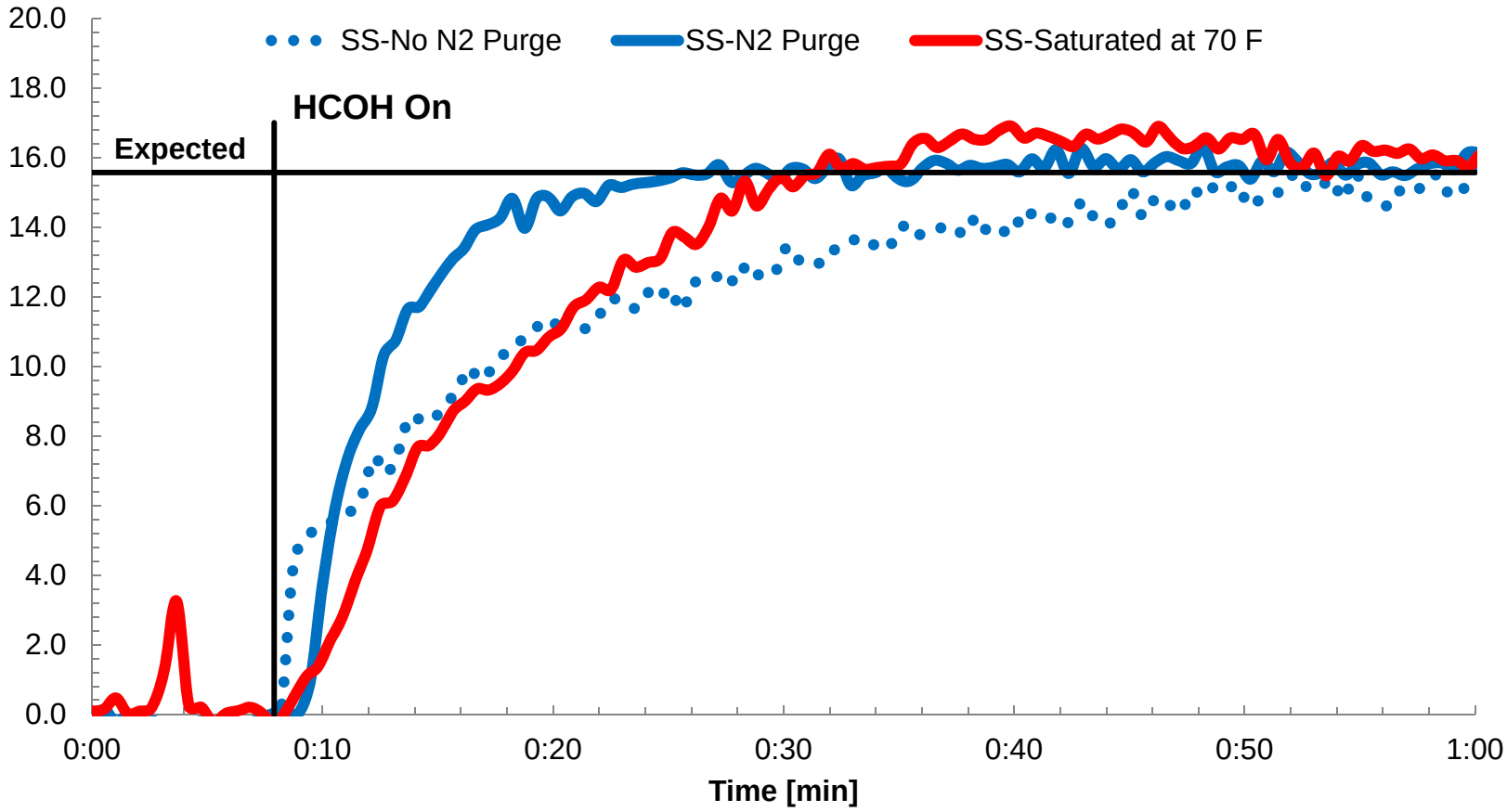
- Initial Regulator Installation
  - Back purge regulator with dry N2
  - Install on tank while still purging
- Pressure/Purge line
  - Close valve to probe, open gas cylinder
  - Close gas cylinder valve, open valve to probe
  - Repeat 10x
- Best practice
  - Leave regulator on cylinder – do not remove.
  - Do not use regulator on any other gas component



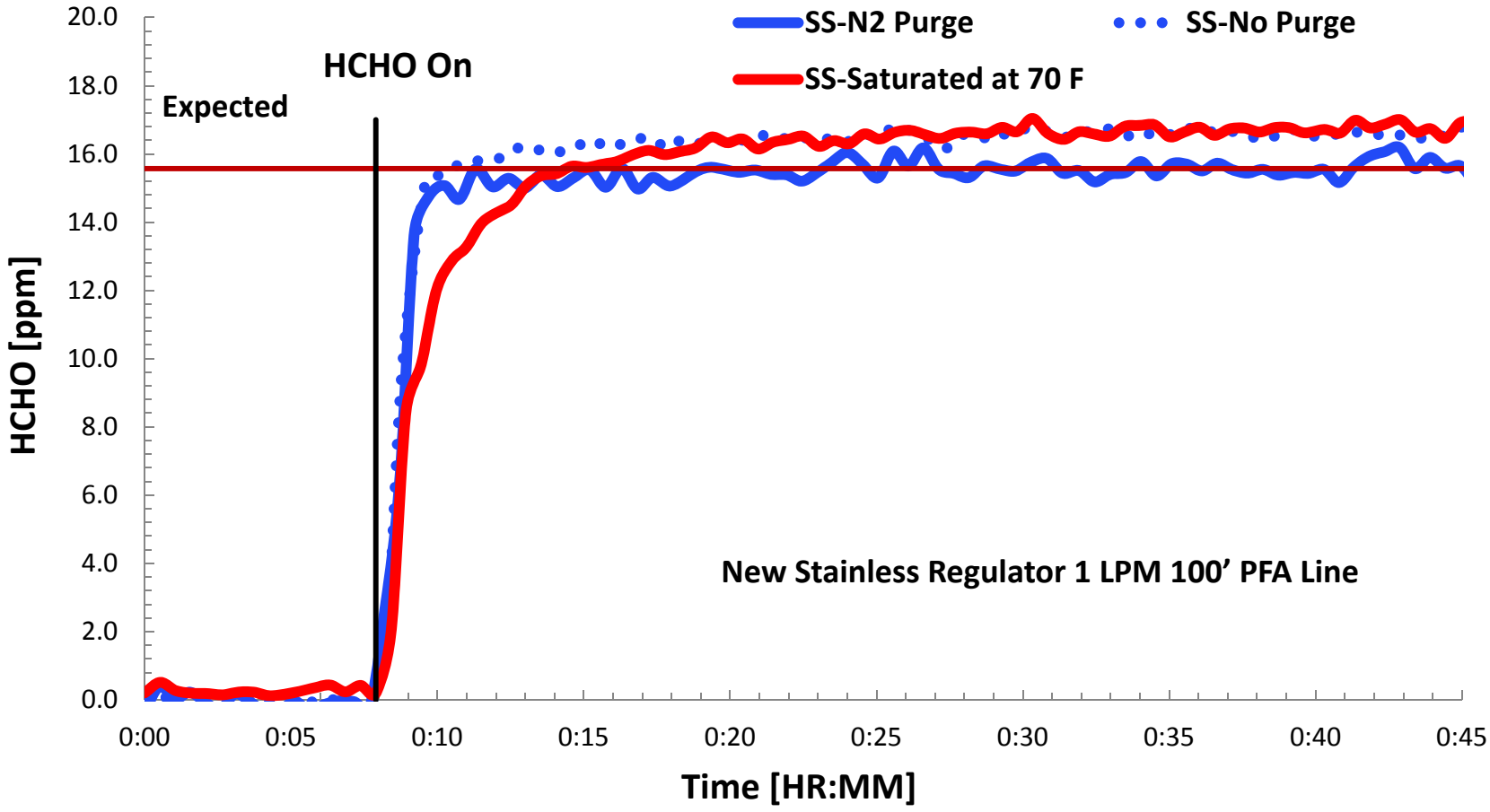
Pressure Regulator NH3 Example



New vs Old Pressure Regulator HCHO Example



New vs Old Pressure Regulator HCHO Example



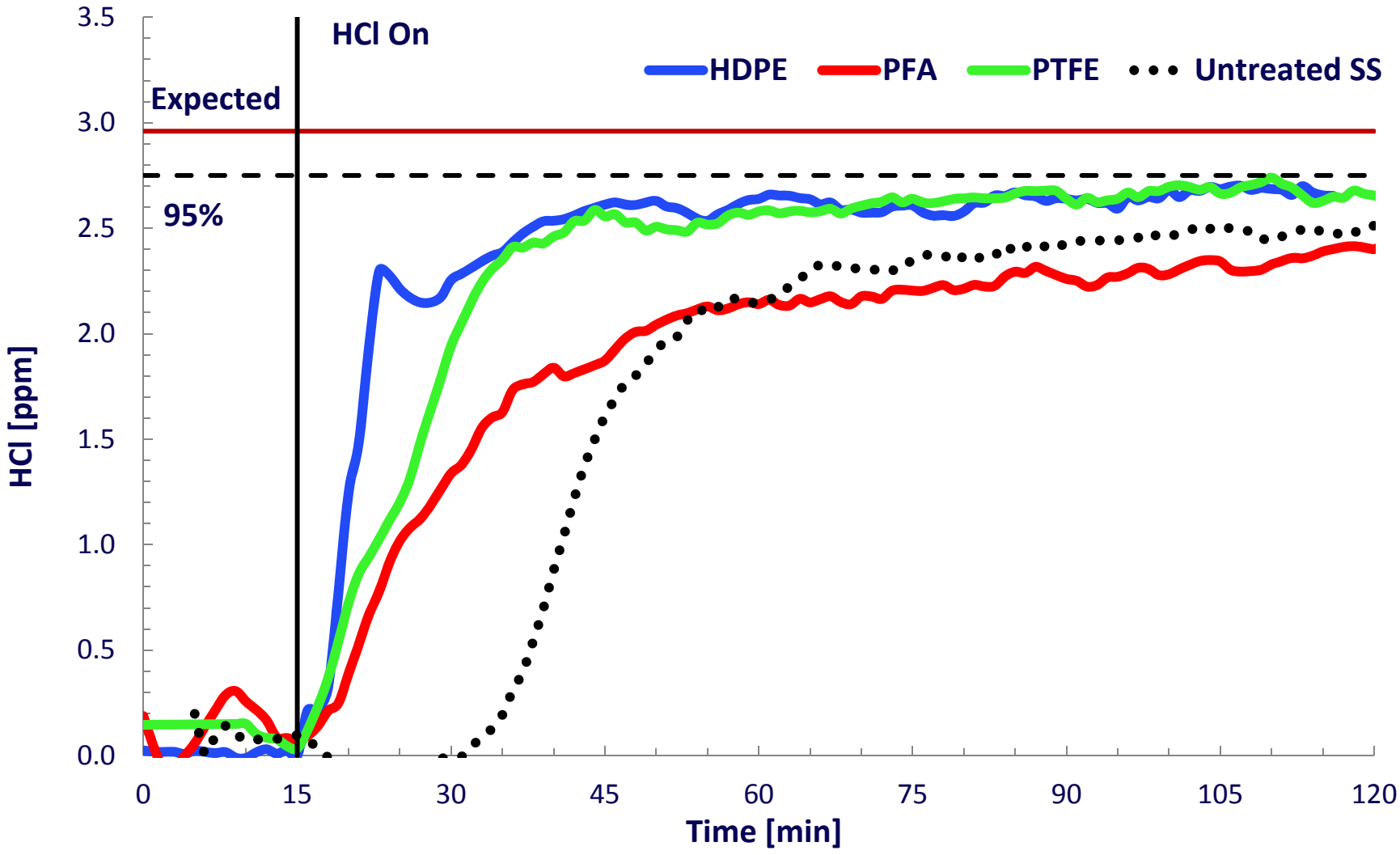
Gas Regulators
What Did We Learn?

- Water in the air can condense in regulator
  - It will absorb NH_3, HF, HCl, NO_2, and CH_2O
  - SilcoNert® Stainless Steel coating
    - Reduces surface adsorption - Good
    - HF reacts with coating - Bad
- Prep required while installing regulator
  - Purge regulator with nitrogen for 15 to 30 minutes
  - Follow with Pressure Purging with cylinder gas 10x
- Avoid using “used” regulators
  - Leave regulator on cylinder all the time
  - Once cylinder expires back purge with N2 while removing

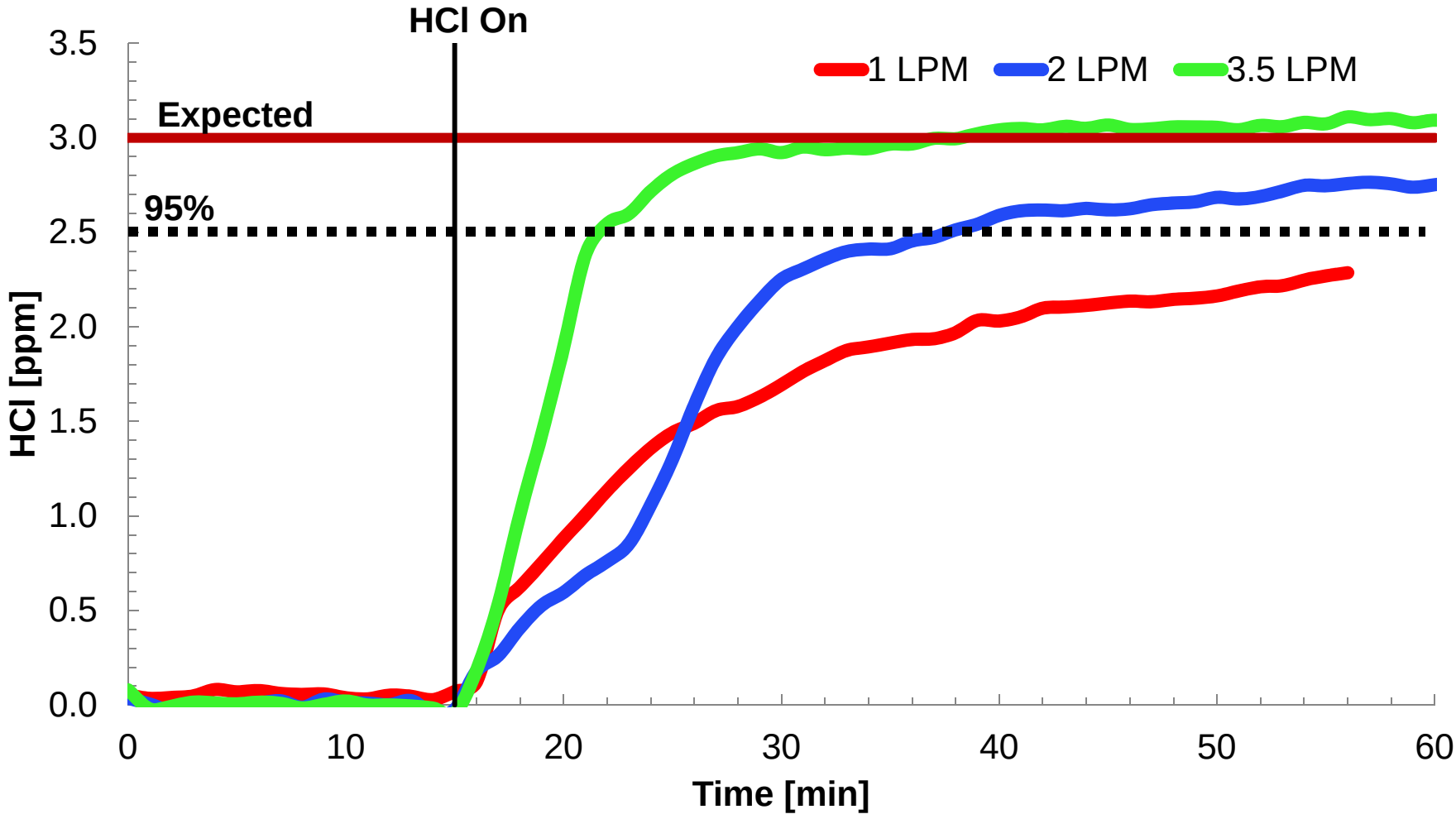
Calibration / Spike Gas Line Material Tests

- Typical materials available
  - Stainless steel (SS)
  - High density polyethylene (HDPE)
  - Poly tetrafluoroethylene (PTFE)
  - Perfluoroalkoxy (PFA)
- Line
  - ¼” Outside Diameter (OD)
  - 100 feet in length
  - Unheated
- Flow rates of 1 to 3.5 LPM

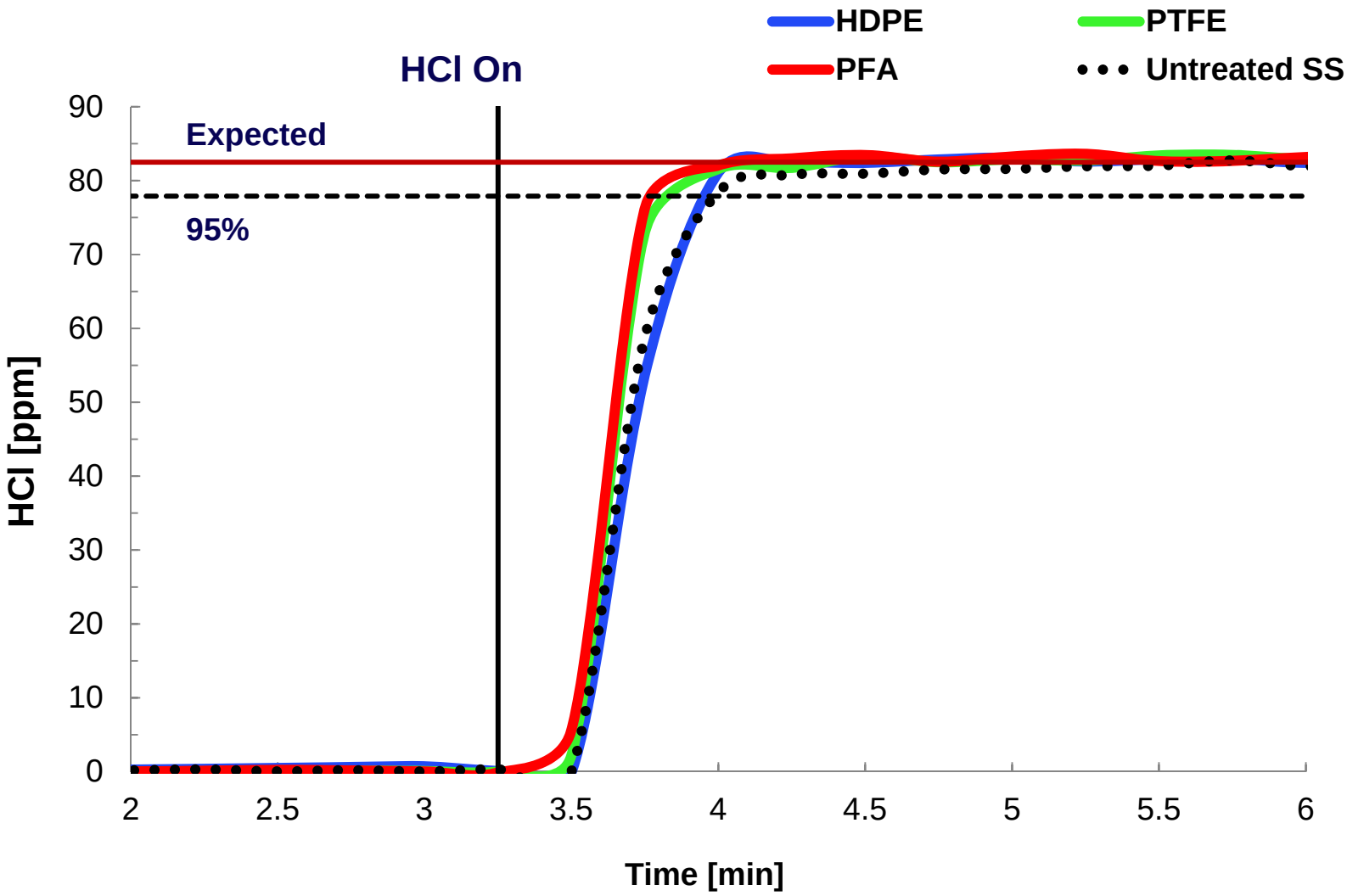
Calibration Line Material
3ppm HCl @ 1LPM



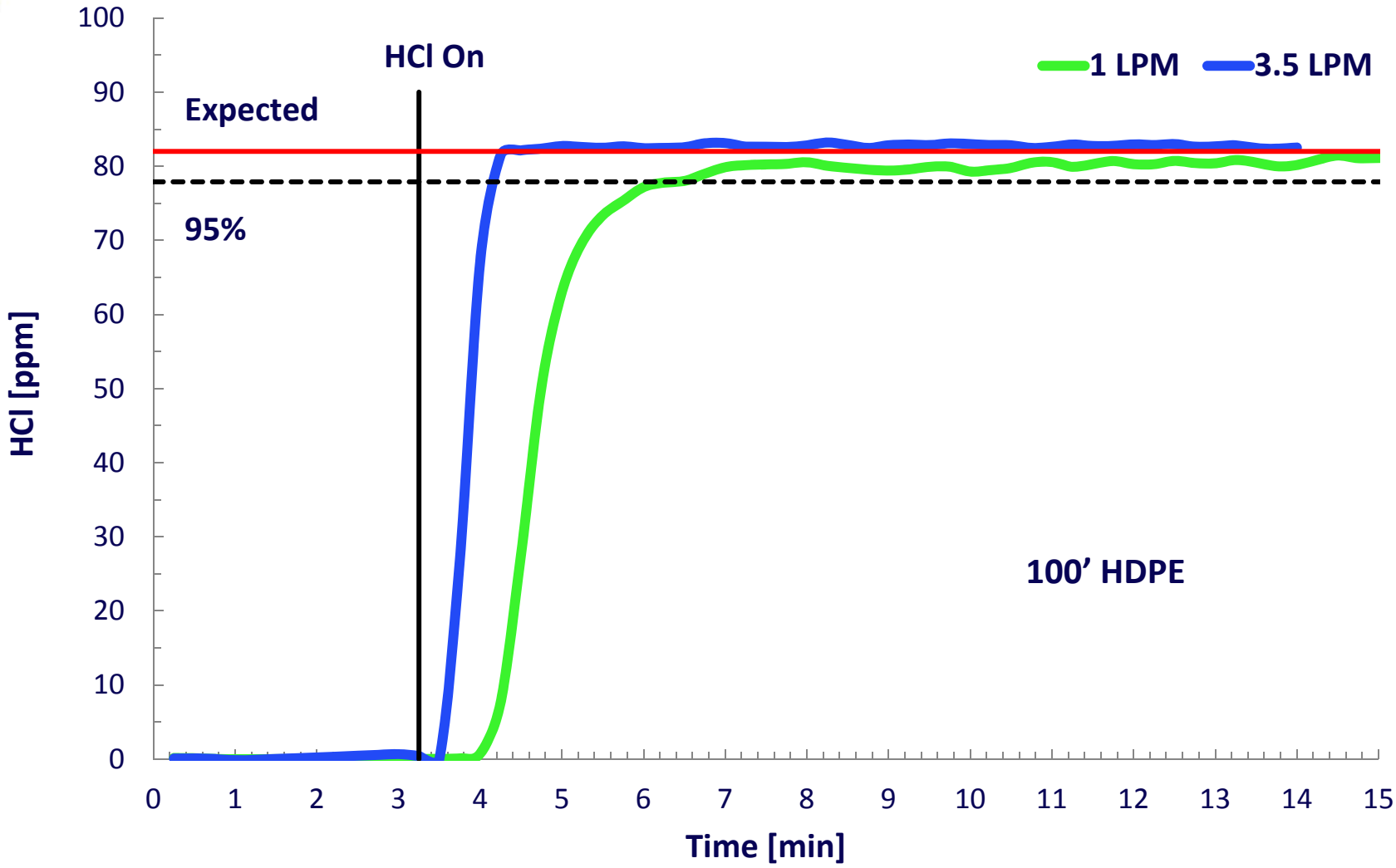
Calibration Line PTFE
3ppm HCl @ Various Flows



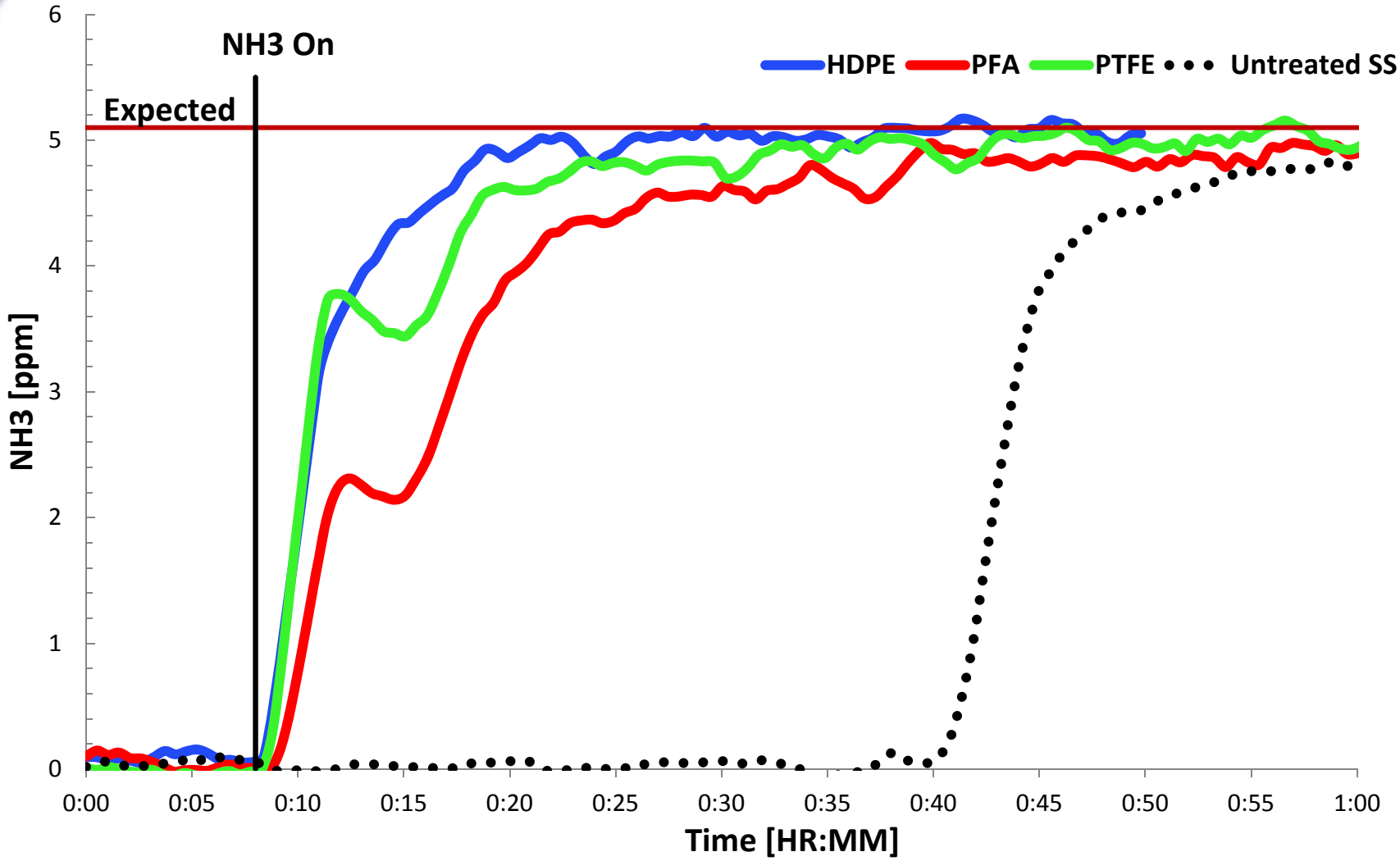
Calibration Line Material
84 ppm HCl @ 3.5LPM



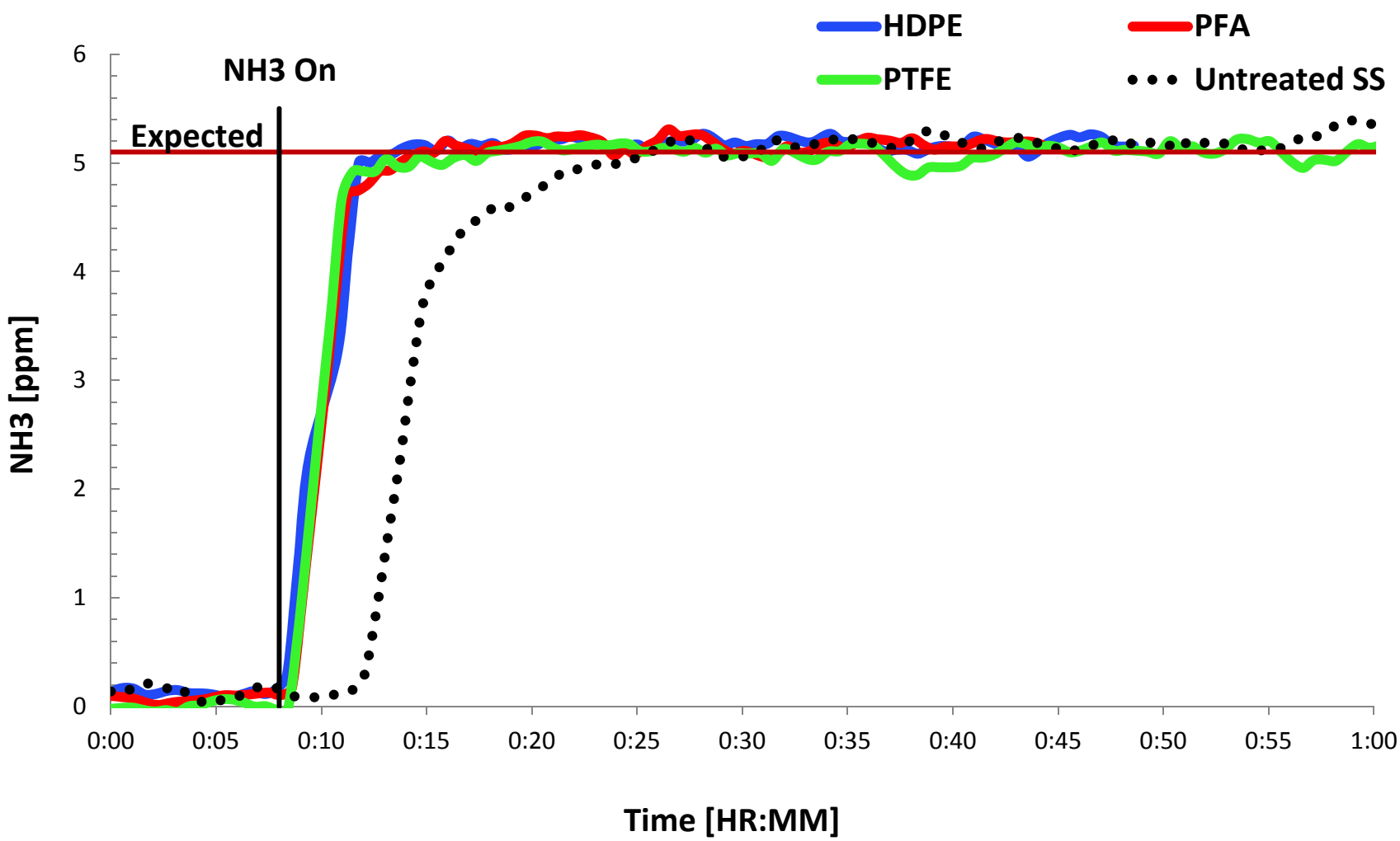
Calibration Line HDPE
84 ppm HCl @ Various Flows



100’ Calibration Line
5ppm NH3 @ 1LPM



Calibration Line Material
5ppm NH3 @ 3LPM



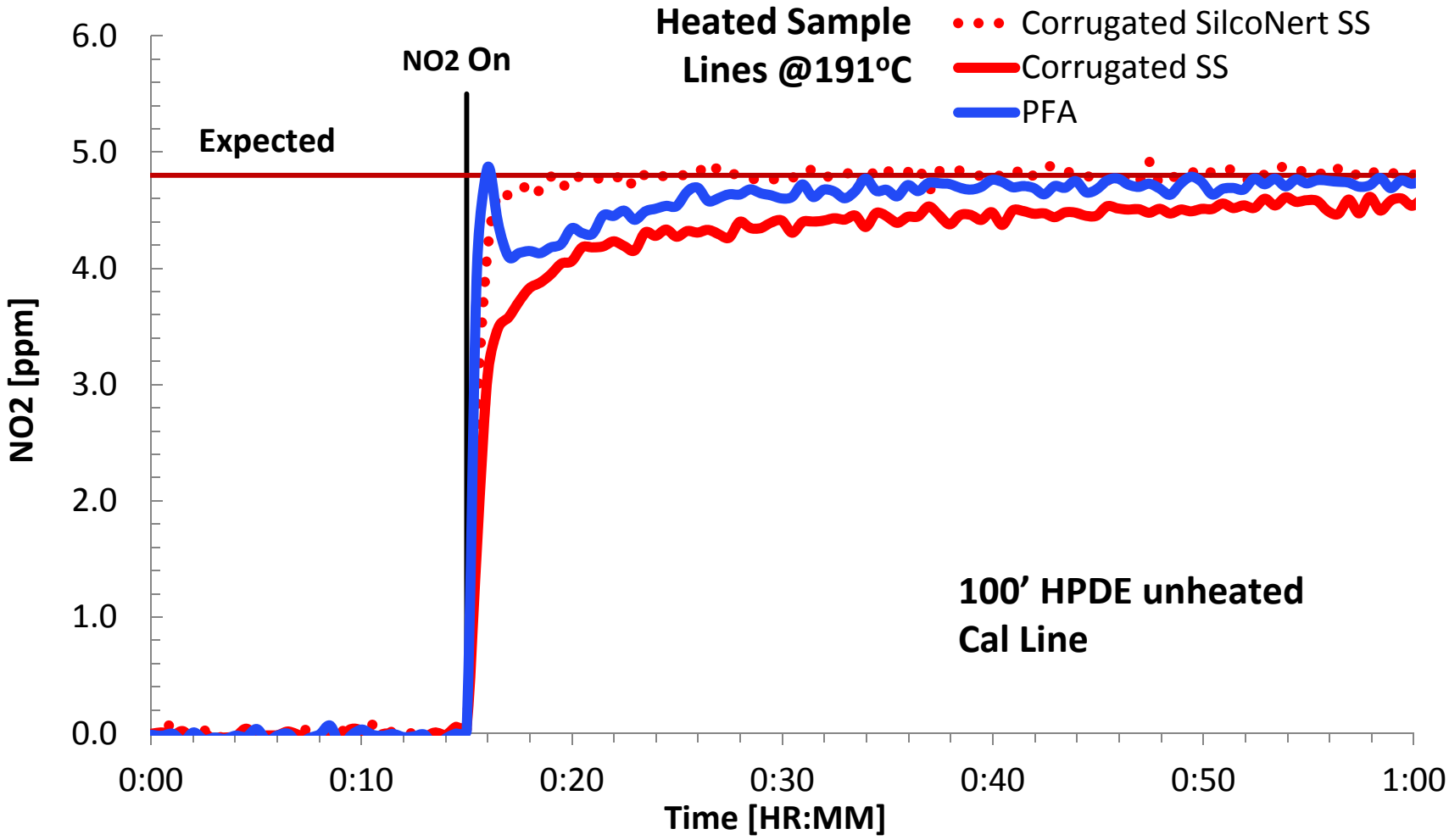
Calibration Lines
What Did We Learn?

- HPDE Lines work fine for all gases
- Flow matters
  - Flow rate >3 LPM is good
- For HCl - use higher concentration cylinders if possible and dilute

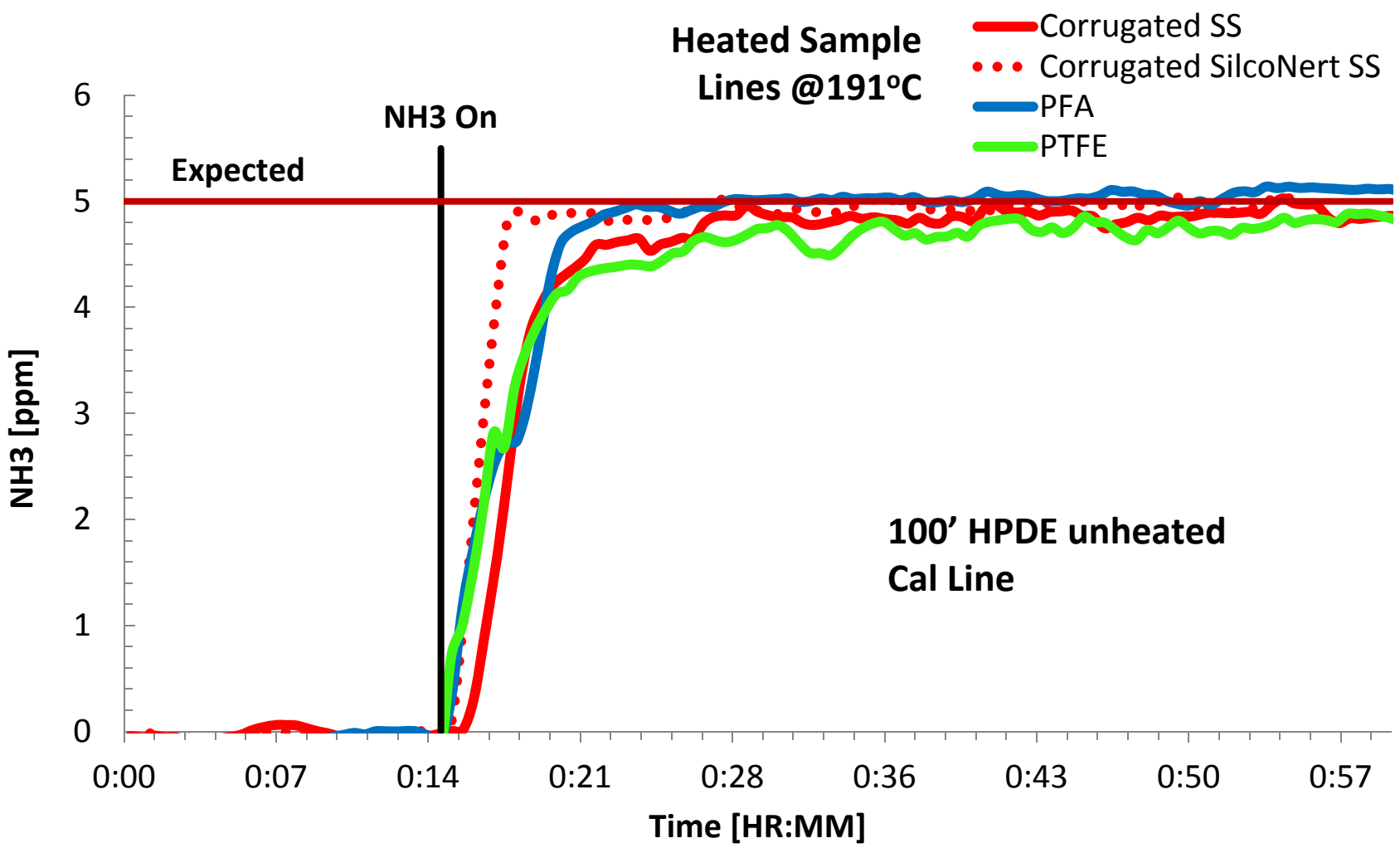
Sample Line Material Test

- Calibration / Spike Line Material
  - 100’ of HDPE - unheated
- Sample Gas Line Material
  - 35’ - Heated to 191 °C
  - PTFE, PFA
  - Stainless Steel
    - Coated with SilcoNert®
    - Uncoated
- Flow rates of 1 to 3.5 LPM using low concentrations

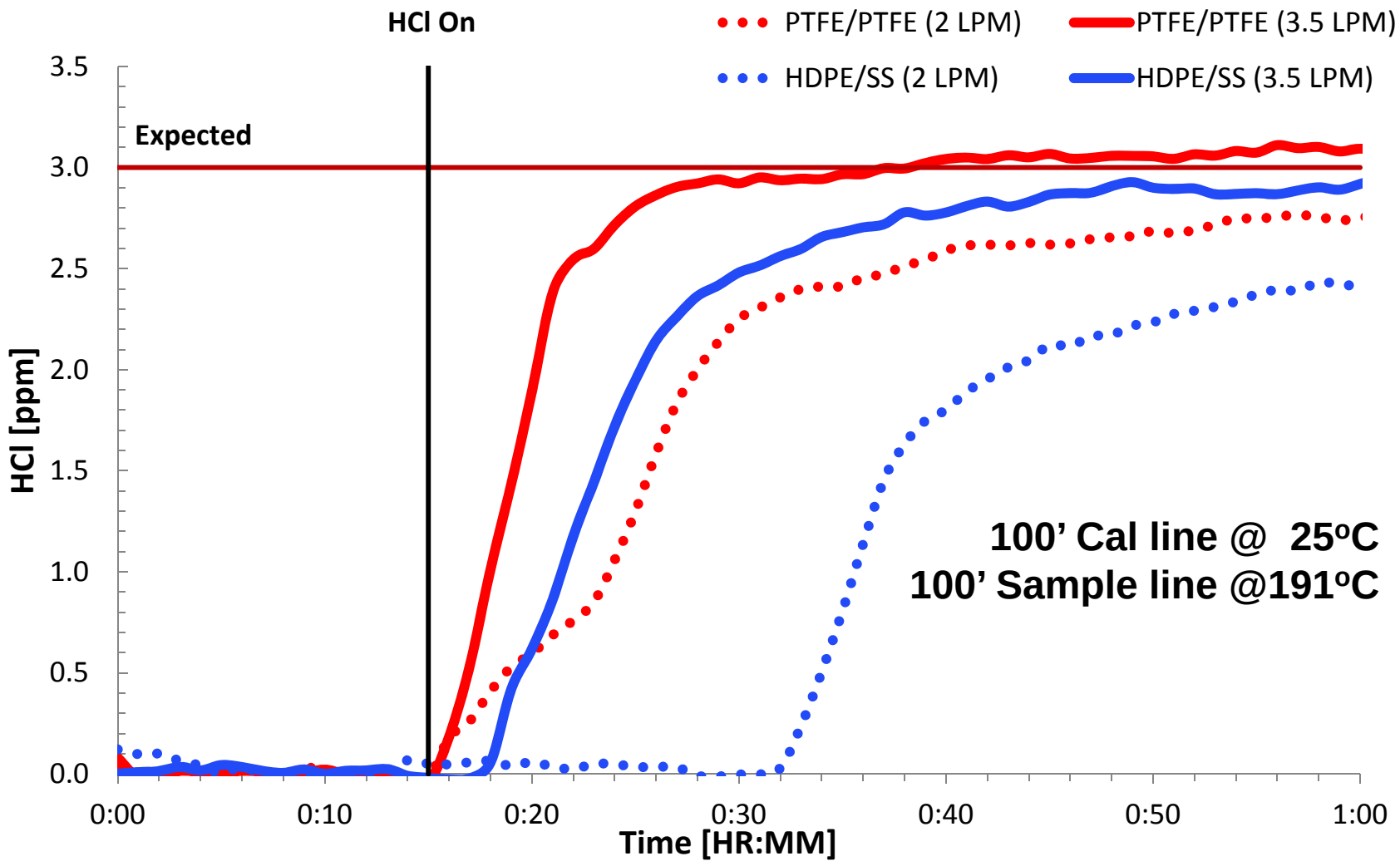
35’ Sample Line Tests ~5ppm NO_2 at 191 °C



35’ Sample Line Tests 5ppm NH_3 at 191 °C



100’ Sample Line and Flow Tests on 3ppm HCl at 191 °C



Heated Sample Lines

What Did We Learn?

- PFA and Silconert SS Lines work well for most gases
- Flow still matters
  - Flow rate >3 LPM is good

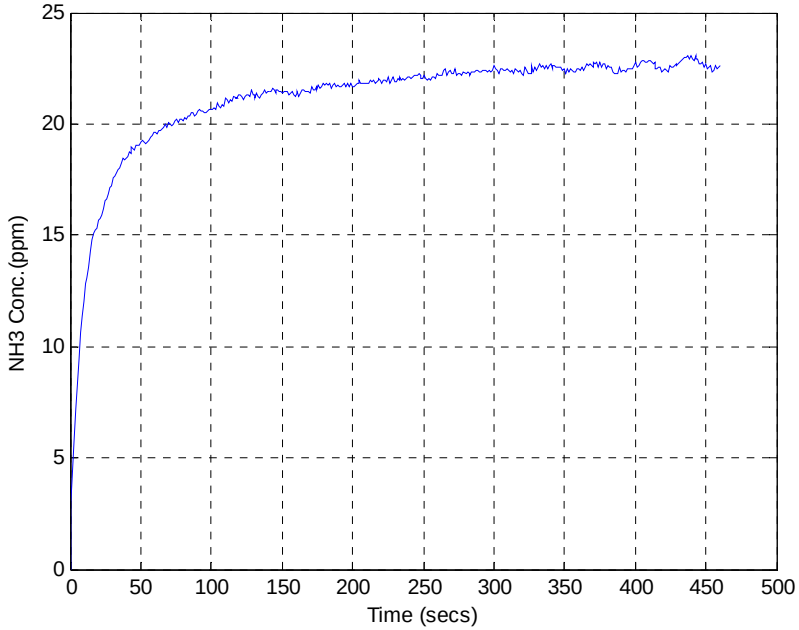
NH_3 Response Testing

- Tests performed at University of Michigan – John Hoard
  - Published in SAE 2014-01-1586 "NH_3 Storage in Sample Lines"
  - Hoard, J., Venkataramanan, N., Marshik, B., and Murphy, B.
- Test Parameters
  - Line Length
    - 20 or 35 feet (6.09 or 10.7 meter)
  - Line Diameter
    - 1/4 or 3/8 inch (6.35 or 9.52 mm)
  - Line Material
    - SS, SS Corrugated, SS Corrugated Siliconert coated, PFA
  - Temperature
    - 113° or 191°C
  - Hydration Effect
    - Dry or Wet (~5% H2O)
  - Flow Rate
    - 5, 10, 15, and 20 SLPM

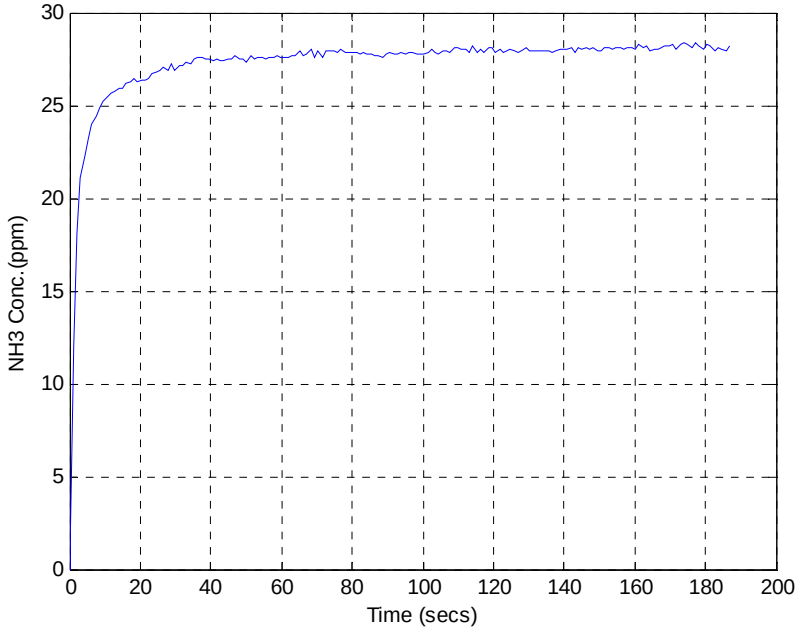
Table of Material Components

Diameter	Sample Lines	
1 / 4 “	**35 feet lines**	
	Line 1	SS Straight
	Line 2	SS Corrugated Silconert
	Line 3	SS Corrugated
	Line 4	Per-Fluro Alkoxy (PFA)
	20 feet lines	
	Line 5	SS Straight
	Line 6	SS Corrugated Silconert
	Line 7	SS Corrugated
3 / 8 “	**35 feet lines**	
	Line 8	SS Corrugated
	Line 9	PFA
	20 feet lines	
	Line 10	SS Corrugated Silconert

Typical “up” Response (NH_3)

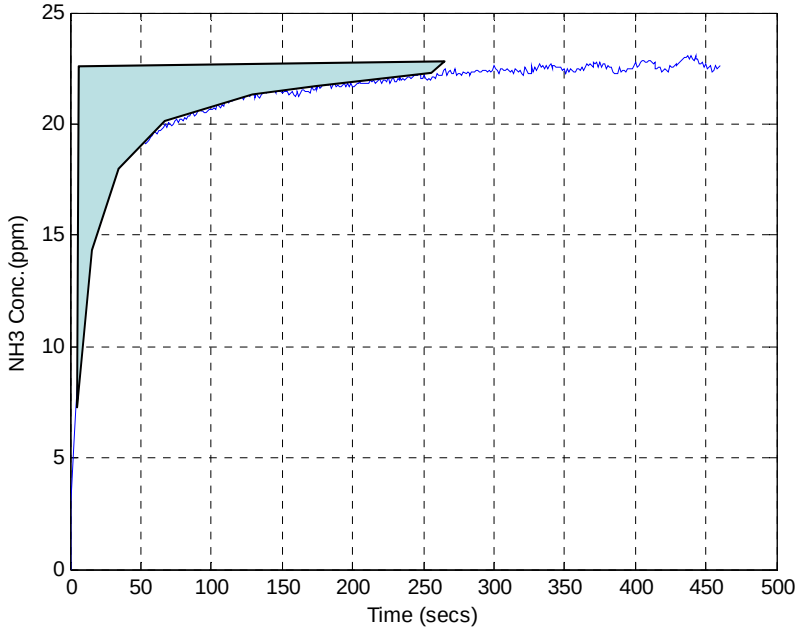


NH3 response of SS Straight line at 113 C 5lpm

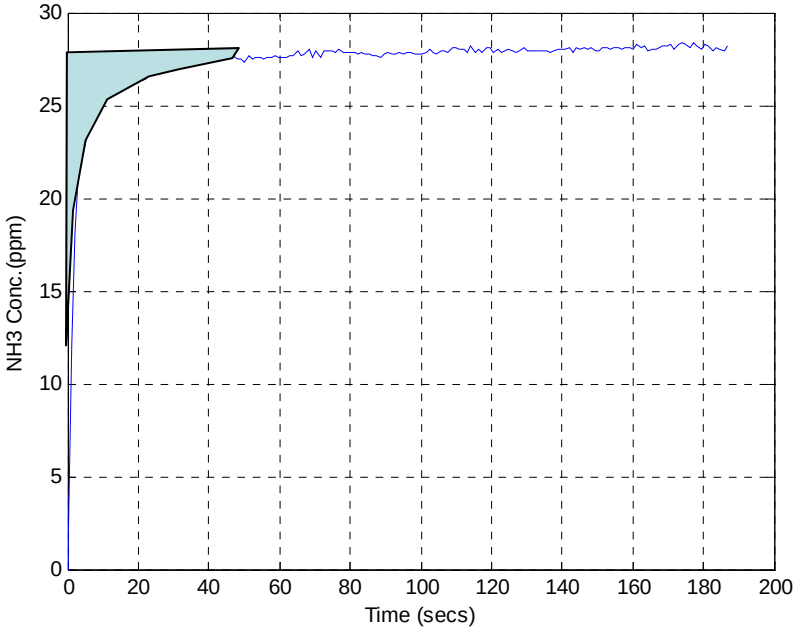


NH3 response of SS Straight line at 113 C 20lpm

NH3 Storage / Retention Area

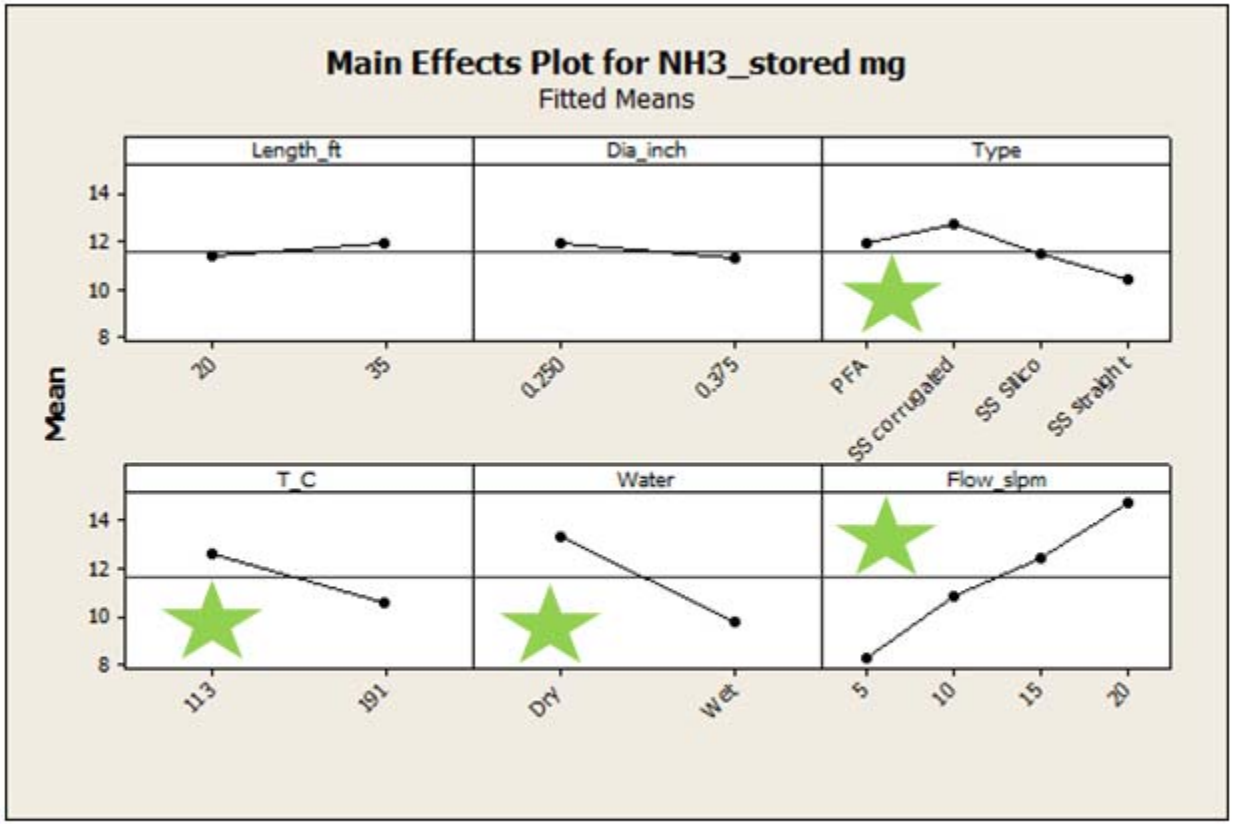


NH3 response of SS Straight line at 113 C 5lpm



NH3 response of SS Straight line at 113 C 20lpm

ANOVA Main Parameters that affect NH_3 Storage



•Significant at 95% confidence

Summary of NH3 Storage / Retention Effects

- For transport and mixing:
  - Flow > 5 SLPM; 10-15 seems a good range
  - Line length and diameter had little effect in this range
  - The sample line type of material: corrugated is slower
- With respect to NH_3 storage/retention effects:
  - Length and diameter not very critical in this range
  - Corrugated line stores most NH_3 straight line least
  - Can be offset by coating corrugated line with Silconert
  - Presence of water reduces NH_3 storage
  - Higher temperature reduces NH_3storage

Line Material Summary

Gas	Calibration Line (25°C)				Sample Line (191°C)			
	PTFE	PFA	HDPE	Stainless Steel	PTFE	PFA	Stainless Steel	SilcoNert® SS
HCl	Very Good	Good	Good	Bad	Very Good	Very Good	Bad	Very Good
NH3	Good	Good	Very Good	Bad	Bad	Good	Good	Very Good
HF	Good	TBD	Good	Bad	Good	TBD	TBD	Bad
HCHO	Good	Very Good	Very Good	Bad	Very Good	Very Good	Very Good	Very Good
NO2	Very Good	Bad	Very Good	Bad	TBD	OK	Bad	Very Good

Sample Probe and Filter Material Summary

Gas	Sample Probe		Filter Material			
	Stainless Steel	SilcoNert® SS	PTFE	Borosilicate Glass	Stainless Steel	SilcoNert® SS
HCl	Good	Very Good	Good	Good	Bad	Bad
NH3	Good	Very Good	OK	Very Good	Good	Very Good
HF	Good	Bad	Good	Bad	Bad	Bad
CH2O	Very Good	Very Good	Very Good	Good	Very Good	Very Good
NO2	Bad	Very Good	Good	Good	Bad	Very Good

Conclusions / Best Practices

- Prep required while installing regulator
  - Purge regulator with nitrogen for 15 to 30 minutes
  - Pressure Purge line with cylinder gas 10x
  - Use new regulators, leave on the cylinder all the time
- Calibration gas wetted surfaces
  - HPDE works fine for all gases
- Sample gas wetted surfaces
  - Silconert coated line and probe best for all except HF
  - Borasilicate glass heated filter material best for all except HF
  - For HF use PTFE heated lines and PTFE filters

BACKUP

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