

## INFLUENCE OF MATERIAL AND TEMPERATURE OF SAMPLING LINES OPERATED UNDER HIGH VACUUM ON THE RESPONSE OF EXTRACTIVE SPECTROMETERS APPLIED TO THE REAL-TIME MEASUREMENT OF TRACE AMOUNTS OF AMMONIA.

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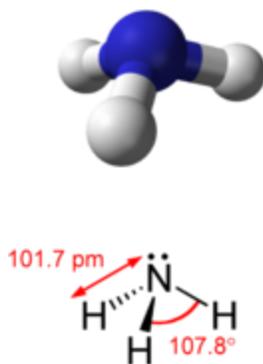
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### ABSTRACT

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Measurement of ammonia (NH<sub>3</sub>) in the emissions of internal combustion engines is a matter of public health protection as excess inhalation of such compound can lead to eye and upper respiratory tract irritation in humans.

Extractive spectroscopy techniques exist that can be used to precisely measure trace concentrations of the compound in various matrices, including raw emissions of internal combustion engines. However, the very chemical nature of this polar molecule presents significant challenges pertaining to the accurate extraction of this molecule from a gas stream to the analyzer.

In addition to obvious precautions such as keeping the extractive sampling line length as short as possible, avoiding water removal (NH<sub>3</sub> is very water soluble), this study proposes a systematic study of the influence of both the nature of the material of the sampling line and of the temperature of said sampling line on the response of the extractive analyzer as measured by the rise and fall times as well as the recovery and purge rates.

A first set of experiments compares response rates using three types of materials (PTFE, Stainless Steel 316L and Sulfinert2000<sup>®</sup> coated SS316L) at fixed temperature, flow rate and sample line length. Relative adsorption / desorption rates of dry NH<sub>3</sub> in these sampling lines are proposed.

A second set of experiments compares analyzer response rates when using PTFE lines at temperatures ranging from 110C to 180C with analyzer response rates when using Sulfinert2000<sup>®</sup>-coated SS316L sampling lines. Results support the fact that temperatures higher than 140C improve rise/fall times and recovery rates, but does not significantly affect purge rates.

Lastly, results of an analytical performance qualification of a TDLAS coupled to a hyper-reflective gas cell and a high-vacuum, room-temperature, Sulfinert2000<sup>®</sup>-coated SS316L ¼" OD sampling line are proposed in support of the claim of fitness of this technological approach for the real-time measurement of NH<sub>3</sub> in internal combustion engines emissions within the scope of current regulatory analytical performance requirements.

## AMMONIA

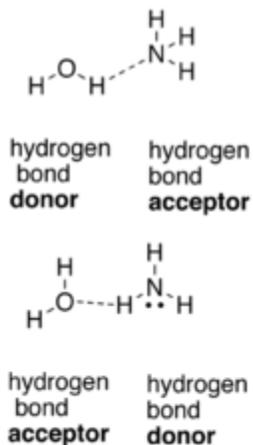


Table 1: H-Bond Enthalpy

Bond	Enthalpy
O-H ••• :N	29 kJ/mol
O-H ••• :O	21 kJ/mol
N-H ••• :N	13 kJ/mol
N-H ••• :O	8 kJ/mol

(Anhydrous) Ammonia is a gas constituted by an atom of nitrogen and three atoms of hydrogen covalently bonded.

From a chemical reactivity view point, the central atom of the molecule is the most interesting. Nitrogen, as a fifth column element, easily combines covalently with proton-donors, yielding a tetrahedral conformation molecule with a free valence electron pair occupying one of its apexes.

This conformation confers the  $\text{NH}_3$  molecule its character as a pure  $\sigma$ -ligand and its propension, second only to  $\text{H}_2\text{O}$  molecules, to engage in very strong electromagnetic inter-molecular interactions of the hydrogen-bonding type.

This hydrogen-bonding capacity is very relevant to the definition of the conditions under which  $\text{NH}_3$  can be sampled in a wet gas mixture and representatively transported to an extractive measurement device. Adsorption of  $\text{NH}_3$  on polymers was first shown by Kosmulski in 2001 <sup>(1)</sup> and later formally quantified by Adam Rose et al. in 2003 (2) who actually proposed a method to calculate the magnitude of the adsorption of  $\text{NH}_3$  on polymer tubing based on a calculated sorption capacity (derived from Langmuir adsorption isotherm and surface reaction rates) and a subsequent equilibrium binding constant dependent of the number of surface sites available for electrostatic bonding. Rose reports statistically significant adsorption of  $\text{NH}_3$  when using LDPE and / or Teflon sampling lines.

Moreover, the presence of water vapor can actually displace  $\text{NH}_3$  H-bonds. As shown in table 1, enthalpies of H-bond involving molecules of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  are such that the increased presence of  $\text{H}_2\text{O}$  will displace  $\text{NH}_3$  from the H-bond, releasing these  $\text{NH}_3$  molecules in the sampling lines, thus yielding an overestimate of  $\text{NH}_3$  each time  $\text{H}_2\text{O}$  concentration increases.

- (1) Kosmulski, M. 2001. *Chemical Properties of Material Surfaces*. Marcel Dekker, Inc. New York, N.Y.  
 (2) Adam J. Rose et al. 2003. *Assessment of Ammonia Adsorption on to Polymer Tubing*. ASAE Annual International Meeting (paper number 034106)

## APPARATUS

### Gas and Gas Delivery

All experiments were performed with recently purchased (< 2 months old) bottles of various concentrations of 1% certified  $\text{NH}_3$ .

Gas delivery control was done using an Environics 4040 gas divider equipped with 4 sulfinert2000<sup>®</sup>-coated mass flow controllers. All gas lines inside the gas divider were also coated with Sulfinert2000<sup>®</sup> to minimize  $\text{NH}_3$  adsorption / desorption phenomena. Precision of the mass flow controllers is provided as 1% of set point by the manufacturer. The MFC's are computer controlled and programs that include automated linearization based on K-factors, densities, and viscosities of both the carrier and the analyte gas were used for gas delivery.

### Sampling Lines

Sampling lines always were 1/4" OD – 1/8" ID, regardless of the material used.

### Spectrometer

A SEMTECH® LASAR calibrated for the measurement of NH<sub>3</sub> was used in all experiments. This analyzer relies on the combination of two patented technologies:

1. Optical Feedback Cavity Enhanced Absorption Spectroscopy (OFCEAS), a direct absorption measurement method using a ring resonator gas cell providing kilometric pathlength with little signal attenuation, thus enabling rapid (10 Hz) measurement of trace concentrations of gases. The technology can be used either with Tunable Diode Lasers (TDL's) or Quantum Cascade Lasers (QCL); however, 40 CFR part 1065 applications can all be successfully done using TDL's in association with that technology.
2. Low Pressure Sampling (LPS) technology, enabling operation of a sampling line at ambient temperature in test cells without risk of gas condensation. It also reduces chemical reaction rates in the sampling line and contributes to an overall improvement of measurement accuracy.

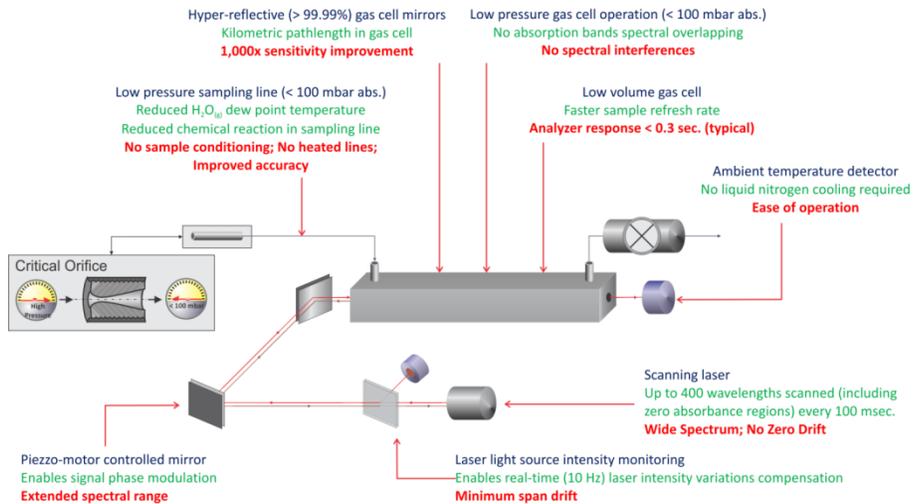


Fig. 1: SEMTECH® LASAR Principle of Operation

### Components Advantages and Benefits (Fig. 1)

**Scanning Laser** – The use of a continuous wave distributed feedback scanning wavelength laser light source enable the measurement of up to 400 data-points spectra every 100 millisecond. The spectra collected include absorption bands for several gases and zero absorbance regions used for auto-zero of the analyzer at 10 Hz.

**Laser Light Source Intensity Monitoring** – Variation of intensity of the light source is one of the most important source of variation (span drift) in a spectrometer. The SEMTECH LASAR laser light source has a built-in beamsplitter redirecting part of the laser beam into a built-in detector, enabling measurement of the variations of light source intensity at 10 Hz. That data is taken into consideration for real-time correction of the variations of light source intensity, reducing span drift of the analyzer.

**Piezzo-motor Controlled Mirror** – The piezzo-motor controlled input mirror enables phase modulation of the laser light beam injected in the hyper-reflective gas cell.

This results in a broadening of the spectral region that can be observed with this type of laser spectrometer, yielding spectra containing up to 400 data points.

Ambient Temperature Detector – The SEMTECH LASAR detector is operated at ambient temperature; temperature regulation is provided by a Pelletier assembly. No liquid nitrogen is required for cooling of the detector, adding to the ease-of-use and operation of this gas analyzer, particularly for in-use applications.

Hyper-reflective Gas Cell Mirrors – The gas cell is not a standard, metric-pathlength, Herriott gas cell. It is a hyper-reflective gas cell (Fabry-Perot resonator) enabling kilometric pathlength. Increasing signal by a factor 1000x not only increases measurement sensitivity proportionally, but it also allows to use Tunable Diode Laser light sources operating in the Near Infrared region of the spectrum without sacrificing the sensitivity of the measurement and/or its applicability to trace concentration gases measurement in the emissions of internal combustion engines.

Low Pressure Sampling (< 100 mbar abs.) – Low pressure sampling is critical to enabling high quality measurement. The benefits of low pressure sampling are: (1) to reduce dew point temperature, allowing operation of the sampling lines at ambient temperature without risk of condensation; in addition to simplifying the operation of the analyzer by not needing heated lines, this also improves sampling accuracy by reducing chemical reaction rates in the sampling line; (2) speeding up sample flow velocity inside the fixed volume 4x6 mm sampling line; and (3) reducing sweep time of the sampling system.

Low Pressure Gas Cell Operation – Operating at very low pressure inside the fixed volume gas cell itself equates to reducing the apparent concentration in gases. The benefit of this operation is that the bandwidth of the absorption bands is narrowed (as per collision band broadening theory) to the point where there is no spectral overlapping, yielding an absence of interferences in the measurement.

Low Volume Gas Cell – The SEMTECH LASAR gas cell is a very low volume gas cell (25 mL). When used in conjunction with very low absolute pressure inside the gas cell, sweep time is significantly reduced when compared to an atmospheric pressure sampling system, resulting in faster instrumental response.

#### **Issue of interferences.**

A spectral range was selected to allow measurement of NH<sub>3</sub> bands in a region where there existed no spectral overlapping. This process was facilitated by the operation of the entire sampling system (including the low volume gas cell) under high vacuum (75 mbar absolute), conditions which significantly narrowed the bandpass of the absorption bands.

**EXPERIMENT 1**

**PTFE vs. Stainless Steel vs. Sulfinert2000®-coated SS316L**

**Experimental:**

- A SEMTECH® LASAR was calibrated for the measurement of NH<sub>3</sub>.
- Three (3) sampling lines were prepared:
  - Dimensions: 1/4" OD – 1/8" ID; 3 meters in length
  - Materials: Sampling line 1 = PTFE  
Sampling line 2 = SS316L  
Sampling line 3 = Sulfinert2000®-coated SS316L
- NH<sub>3</sub> was first released directly into the spectrometer gas inlet port to establish a baseline response time. Then, NH<sub>3</sub> was released into the spectrometer via each of the three sampling lines.
- All analysis performed at room temperature using a bottle of 11.5 ppm NH<sub>3</sub>, with 5 replicate assays for each type of lines.

**Results:**

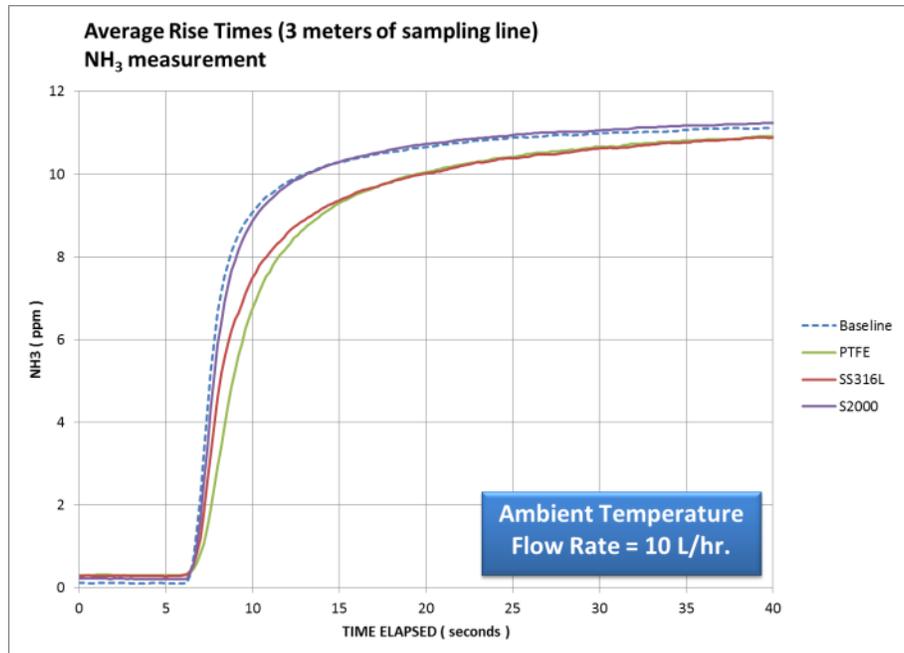


Fig. 2a: Average rise times for measurement of NH<sub>3</sub>

Figure 2a illustrates the average rise times (at very low flow rate) measured using each of the three types of lines and the intrinsic response rate of the analyzer at 10 liter/hour flow rate when operated at 75 mbar.

Actual average rise times are:

Sampling Line Material	Average Rise Time (T <sub>10-90</sub> )
None (intrinsic analyzer response)	8.8 seconds
PTFE	16.2 seconds
SS316L	17.0 seconds
Sulfinert2000®-coated SS316L	8.4 seconds

The use of either PTFE or SS316L lines doubles the rise time of analyzer response for NH<sub>3</sub> measurement. However, the use of a 3-meter Sulfinert2000®-coated SS316L line has no statistically significant impact on the analyzer response time, suggesting that no significant adsorption on NH<sub>3</sub> molecules occurred in the sampling line.

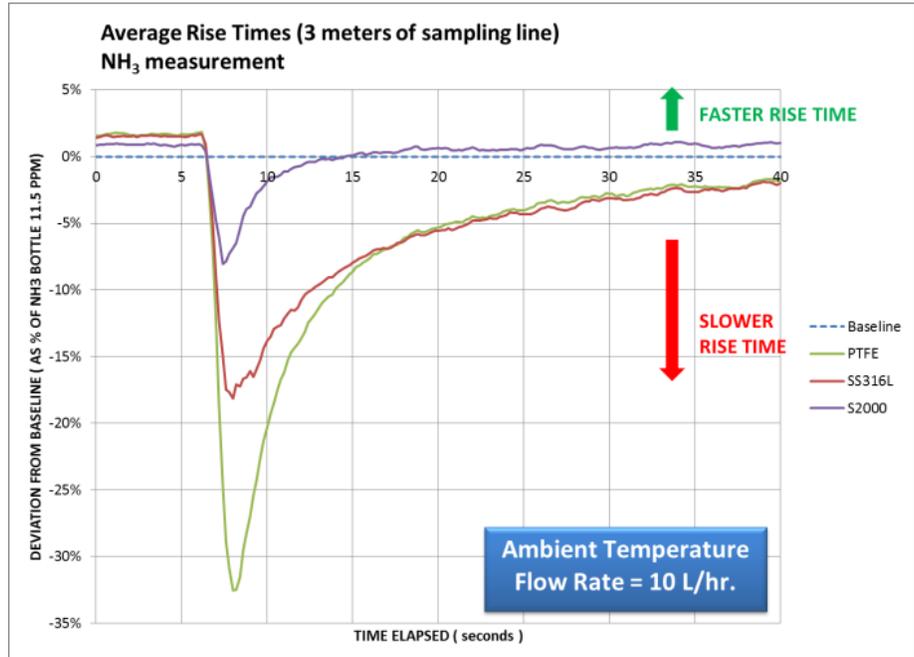


Fig. 2b: Rise times for measurement of NH<sub>3</sub> expressed relatively to the intrinsic response rate of the analyzer

Figure 2b represents the concentration of NH<sub>3</sub> measured as a function of time, expressed as a percentage of the NH<sub>3</sub> measured by the instrument when not using a sampling line. This relative measurement provides a more finely resolved picture of the retention of NH<sub>3</sub> in the sampling lines as a function of time. We observe:

- A 32.55% deficit in NH<sub>3</sub> measured at initial rise time when using the PTFE line;
- A 18.15% deficit in NH<sub>3</sub> measured at initial rise time when using the SS316L line; and
- A 8.07% deficit in NH<sub>3</sub> measured at initial rise time when using the Sulfinert2000®-coated SS316L line.

These under-estimates of NH<sub>3</sub> measurement are directly proportional to the amount of NH<sub>3</sub> that is adsorbed in the sampling line. It is interesting to note that, despite very similar final T<sub>10-90</sub> times, this finer approach shows that NH<sub>3</sub> is much more important in the PTFE line than it was in the SS316L line. It also shows that the Sulfinert2000® solution is not absolute and that some retention of NH<sub>3</sub> still occurs, albeit much less than with the other two types of lines.

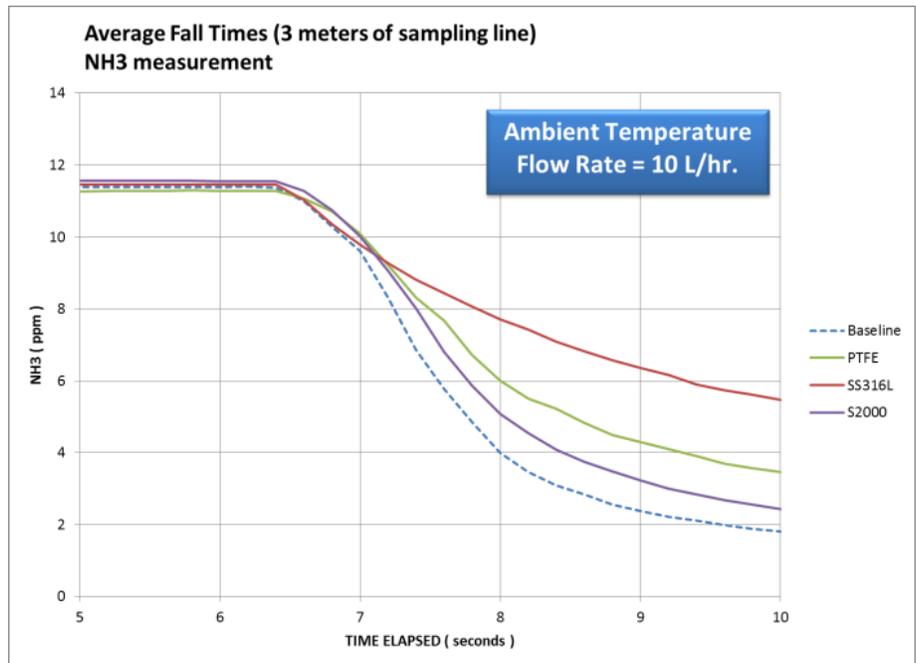


Fig. 2c: Average fall times for measurement of NH3

Figure 2c illustrates the average fall times (at very low flow rate) measured using each of the three types of lines and the intrinsic response rate of the analyzer at 10 liter/hour flow rate when operated at 75 mbar. Actual average rise times are:

Sampling Line Material	Average Fall Time (T <sub>100-10</sub> )
None (intrinsic analyzer response)	6.0 seconds
PTFE	18.2 seconds
SS316L	33.0 seconds
Sulfinert2000®-coated SS316L	9.4 seconds

The use of PTFE triples fall time and the use of SS316L quintuples fall time of analyzer response for NH<sub>3</sub> measurement. Using the Sulfinert2000®-coated SS316L line has a detectable impact on the analyzer fall time (1.5x), suggesting that some NH<sub>3</sub> molecules adsorption still occurs in the sampling line, as was suggested by the results shown in figure 2b.

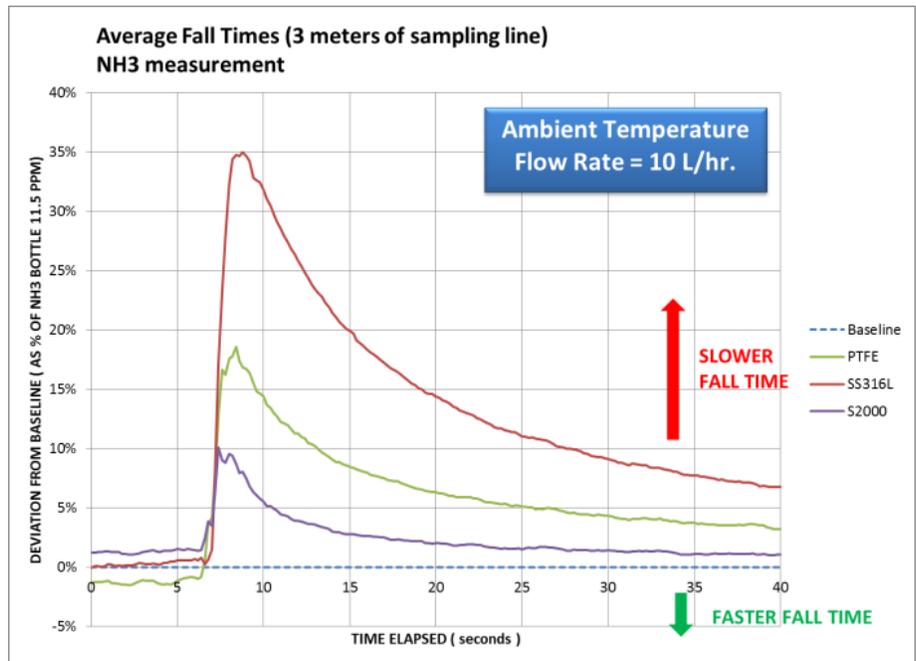


Fig. 2d: Fall times for measurement of NH<sub>3</sub> expressed relatively to the intrinsic response rate of the analyzer

Figure 2d represents the concentration of NH<sub>3</sub> measured as a function of time, expressed as a percentage of the NH<sub>3</sub> measured by the instrument when not using a sampling line. This relative measurement provides a more finely resolved picture of the retention of NH<sub>3</sub> in the sampling lines as a function of time. We observe:

- A 18.11% over-estimate in NH<sub>3</sub> measured at initial fall time when using the PTFE line;
- A staggering 34.70% over-estimate in NH<sub>3</sub> measured at initial fall time when using the SS316L line; and
- A 10.11% over-estimate in NH<sub>3</sub> measured at initial fall time when using the Sulfinert2000<sup>®</sup>-coated SS316L line.

These over-estimates of NH<sub>3</sub> measurement are directly proportional to the amount of NH<sub>3</sub> that is adsorbed in the sampling line. A surprising result is how much more difficult it is to purge out adsorbed NH<sub>3</sub> from the SS316L line than it is to purge it out of the PTFE line. Perhaps this is due to different type of interactions between NH<sub>3</sub> molecules and the material. However, the Sulfinert2000<sup>®</sup> solution, if not perfect, remains the one sampling line material choice with the least impact on analyzer response time.

As a conclusion to this first study, we selected the following line material and operational conditions for all subsequent experimentation pertaining to NH<sub>3</sub> measurement:

- |                          |   |   |
|--------------------------|---|---|
| Material                 | = | Sulfinert2000 <sup>®</sup> -coated SS316L |
| Temperature of operation | = | ambient                                   |
| Pressure of operation    | = | 75 mbar                                   |
| Flow rate                | = | minimum 10 Liter / hour                   |

## EXPERIMENT 2

### Heated PTFE (110 – 191C) vs. Sulfinert2000®-coated SS316L (@25C)

#### Experimental:

- A SEMTECH® LASAR was calibrated for the measurement of NH<sub>3</sub>.
- Two (2) sampling lines were prepared:
  - Dimensions: 1/4" OD – 1/8" ID; 3 meters in length
  - Materials: Sampling line 1 = heated PTFE.  
Sampling line 2 = Sulfinert2000®-coated SS316L
- For each level of temperature, 10 consecutive injection of NH<sub>3</sub> followed by 10 consecutive injections of dry N<sub>2</sub> were completed, each injection lasting 3 minutes to allow for stabilization of the analyzer response (see Fig. 3)
- All analysis performed using a bottle of 102.5 ppm NH<sub>3</sub>.

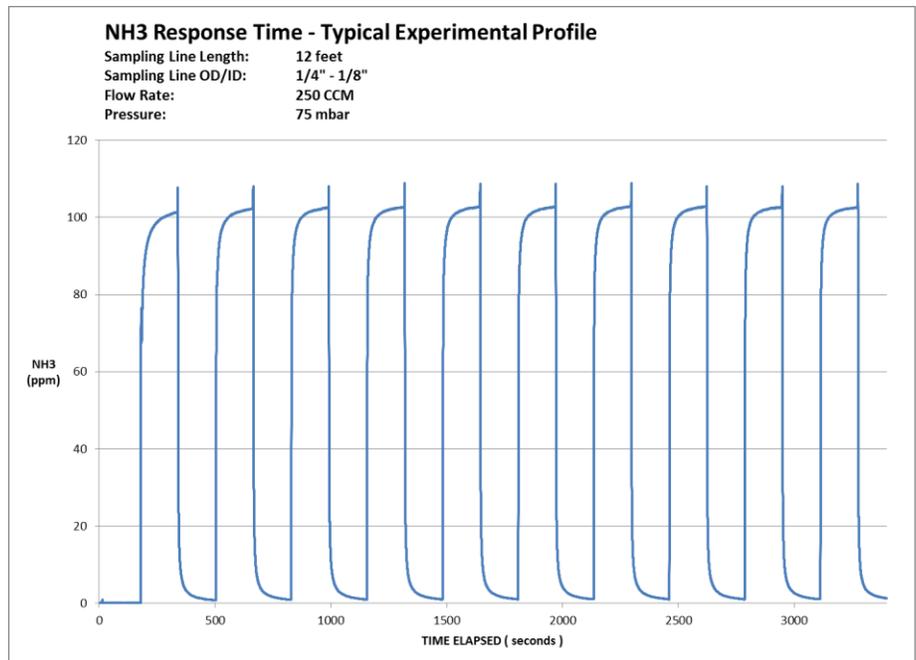


Fig. 3: Typical experimental profile; 10 consecutive injections of NH<sub>3</sub> followed by immediate injections of dry N<sub>2</sub>.

#### Results:

All individual results are reported as figures A-1 through A-10 in appendix 1 of this document.

There are no results reported for experiments with PTFE line at temperatures 120C and 191C due to technical problems with the gas divider during these 2 experiments.

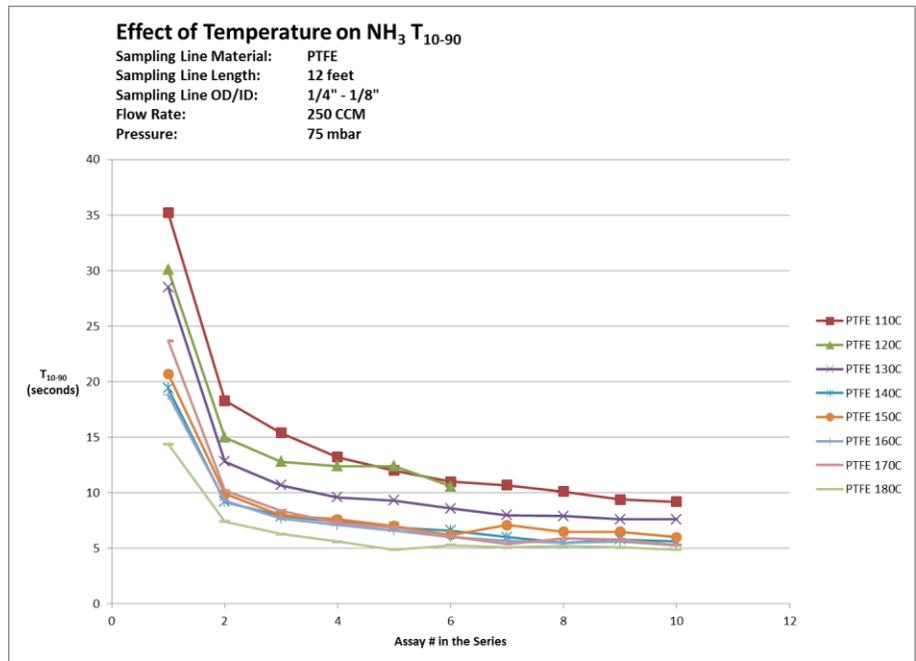


Fig. 4a: effect of temperature on NH<sub>3</sub> rise time using PTFE lines

Figure 4a reports the T<sub>10-90</sub> measured for all 10 assays at all temperatures tested.

A first observation is that there seems to be a wetting / NH<sub>3</sub> saturation effect occurring with the PTFE line, regardless of the temperature at which they are operated. As a result of this observation, only the last 4 observations of each series are taken into consideration when comparing the rise / fall time performances of the PTFE lines at various temperatures with that of the sulfinert2000®-coated sampling lines.

A second observation is that rise time, regardless of the assay number in the series, seems to improve when temperature increases until sampling line temperature reaches 150°C. Then, there seems to be no statistically significant improvement in rise time as temperature further increases.

This suggests that, if using a PTFE line, best rise times would be obtained at temperature of no less than 150°C. However there is no need to further increase temperature from that point on, therefore avoiding to further increase another source of inaccuracies in sampling: chemical reaction rates in the sampling line.

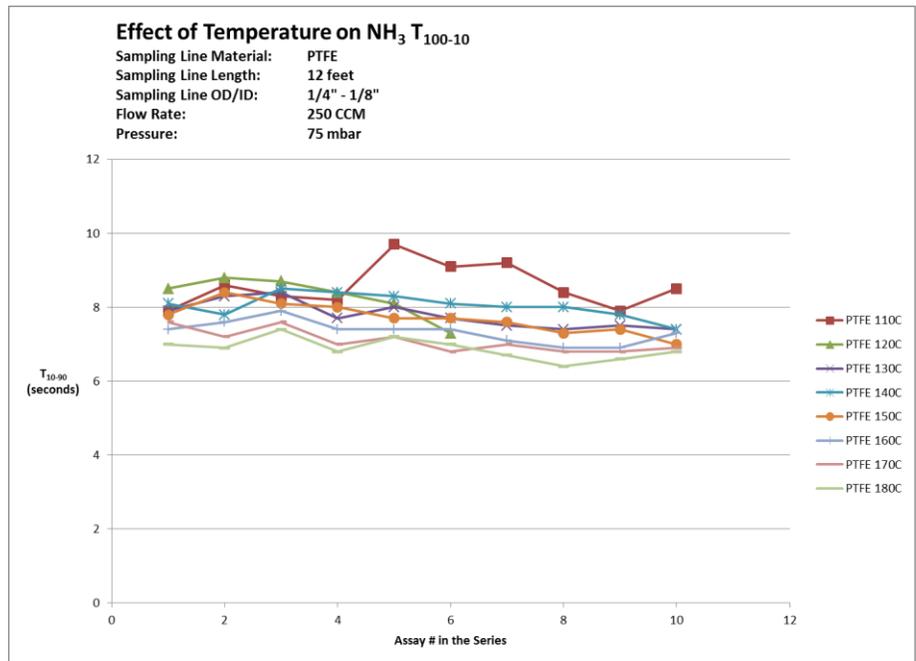


Fig. 4b: effect of temperature on NH<sub>3</sub> fall time using PTFE lines

Figure 4b reports the T<sub>100-10</sub> measured for all 10 assays at all temperatures tested. At the difference of what was observed during the rise time experiments, there seems to be no wetting / NH<sub>3</sub> de-saturation effect occurring with the PTFE line as the fall times at a given temperature remain quite similar, regardless of the position of the assay in the series.

A second observation is that temperature seems to have little effect on fall time. One could argue a very slight improvement in fall time when the PTFE sampling line temperature is increased, however, the statistical significance of this observation remains in doubt based upon that data set.

This suggests that, regardless what temperature would be selected for operation of the sampling line based on other criteria, when operated under the above-described thermodynamic conditions, the PTFE line can be operated at that temperature without making fall times worse. This parameter is essentially a non-contributor to the selection of an optimum PTFE sampling line operating temperature.

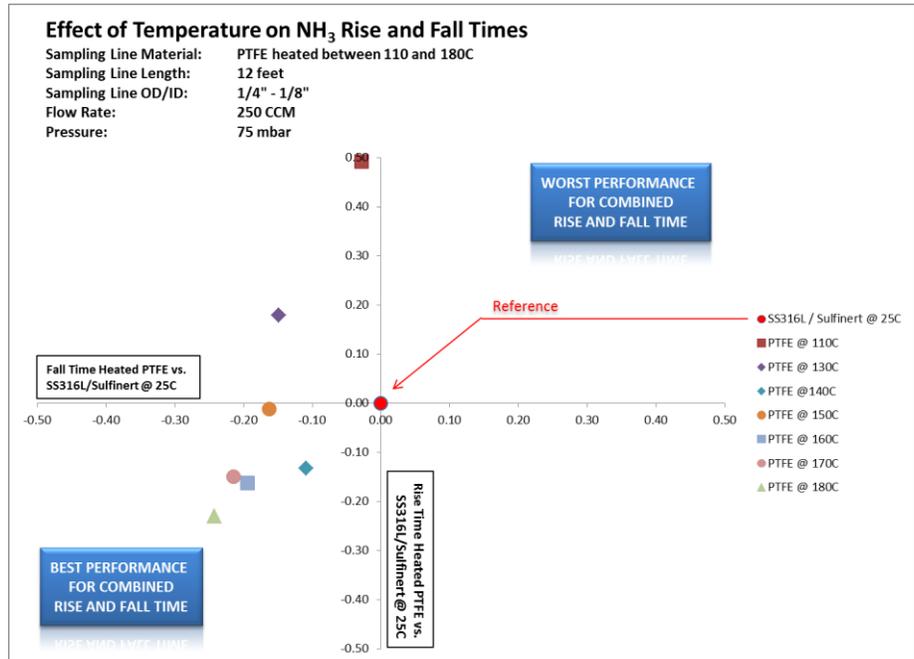


Fig. 4c: effect of temperature on NH<sub>3</sub> combined rise and fall times using PTFE lines expressed as a function of the rise/fall time observed using a Sulfinert2000®-coated SS316L operated at room temperature.

Figure 4c attempts to simplify the selection process for an optimum temperature of operation of a PTFE line when comparing that performance to that of a Sulfinert2000®-coated sampling line operated at room temperature.

X-Axis carries fall time performance information and Y-Axis carries rise time performance information.

As no data point makes it into the upper- and lower right quadrant of the graph, we can report that heated PTFE sampling lines allowed for slightly better fall times than when using the Sulfinert2000®-coated SS316L line.

Additionally, this graph further confirms the observation made for fig. 4a, i.e. that it takes heating the PTFE line improves rise time. It also appears that this temperature must be at least 150°C in order to equal the rise time performance of a Sulfinert2000®-coating SS316L line operated at room temperature. At the difference of the observation derived from Fig. 4a and 4b, this more discriminating method allows us to clearly see that the combination rise / fall times keeps improving as temperature of the sampling line keeps increasing (at least up to 180°C, the highest validated set of data points used in this experiment.)

From these observations, it seems that:

- a high temperature (at least 180°C confirmed, perhaps 191°C if it were confirmed) is recommended for the best response time performance of the NH<sub>3</sub> analyzer connected to the line.
- A PTFE line heated @ 180°C offers a slight advantage to a Sulfinert2000®-coated SS316L sampling line operated at room temperature in terms of response rate. However, this selection criterion would have to be weighed against that of the greatly increased chemical reaction rate in the sampling line operated at high temperature when deciding on a final material / temperature of operation for the sampling system.

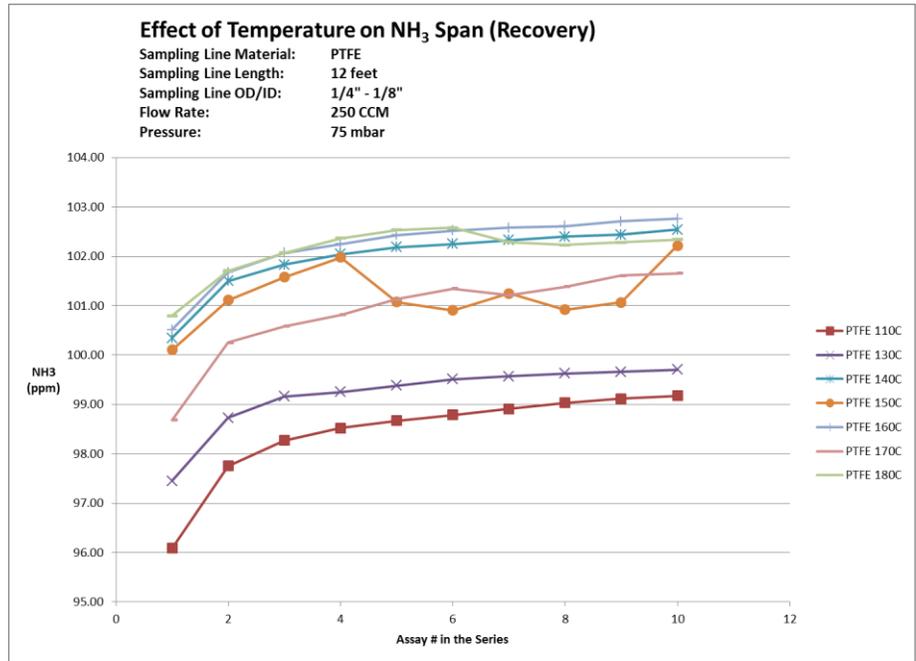


Fig. 5a: effect of temperature on NH<sub>3</sub> recovery using PTFE lines

Figure 5a reports the actual concentration of NH<sub>3</sub> measured for all 10 assays at all temperatures tested.

As for the rise time chart (Fig. 4a), we confirm that a wetting / NH<sub>3</sub> saturation effect must be occurring with the PTFE line, regardless of the temperature at which they are operated. The effect is more pronounced at lower temperatures, suggesting more resilient adsorption (or less active desorption) occurring at lower temperatures of the PTFE line.

A second observation is that it takes a temperature of at least 160°C for the measured NH<sub>3</sub> concentration to come within 2% of the actual bottle value; The choice of 2% error here is a value consistent with the combined 1% bottle precision and the 1% of set point mass flow controller precision.

This suggests that, if using a PTFE line, acceptable recovery rates can only be reached at temperatures of 160°C or more.

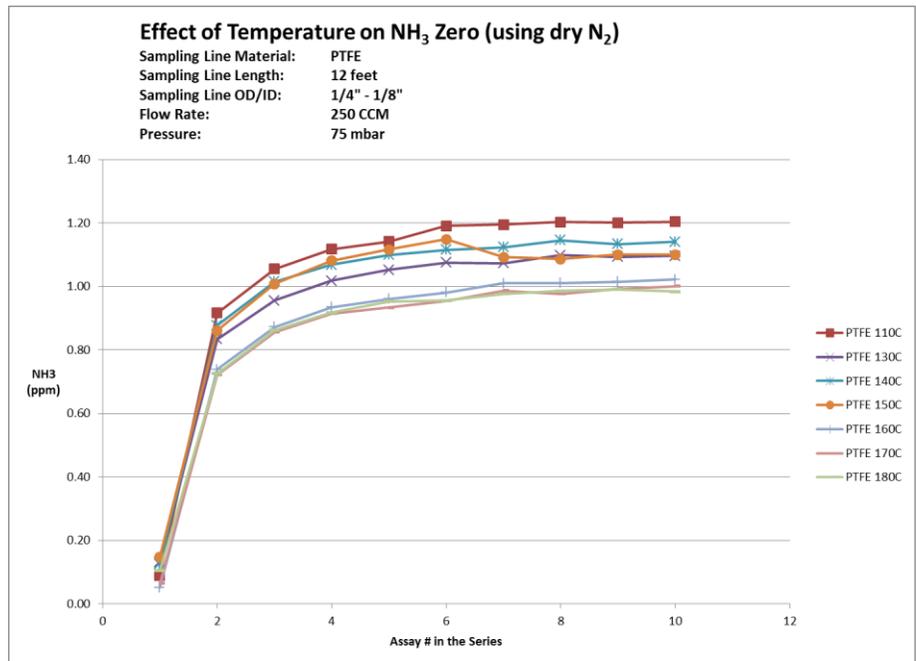


Fig. 5b: effect of temperature on residual NH<sub>3</sub> in PTFE lines when using dry N<sub>2</sub> as purge gas.

Figure 5b reports the zero readings of the system after flowing N<sub>2</sub> for 2 minutes as measured for all 10 assays at all temperatures tested.

The first data point at all temperatures (assay #1) reports the zero reading measured before any NH<sub>3</sub> was injected into the system; it must be noted that the entire system was purge with dry N<sub>2</sub> for at least 1 hour after each experiment.

Regardless of the temperature of operation of the PTFE line, after 2 minutes of dry N<sub>2</sub> purge, there always seems to be a residual 1 or so ppm of NH<sub>3</sub> that lingers in the system.

The phenomenon appears to become somewhat attenuated when temperature of the sampling line rises, with residual NH<sub>3</sub> concentrations steadily decreasing from 1.2 ppm when operating the line at 110°C to 1.0 ppm when operating the PTFE sampling line at 160°C or more.

This suggests that, regardless what temperature would be selected for operation of the sampling line based on other criteria, when operated under the above-described thermodynamic conditions, the PTFE line creates a systematic source of error in the measurement, measured under these above conditions to be approximately 1 ppm.

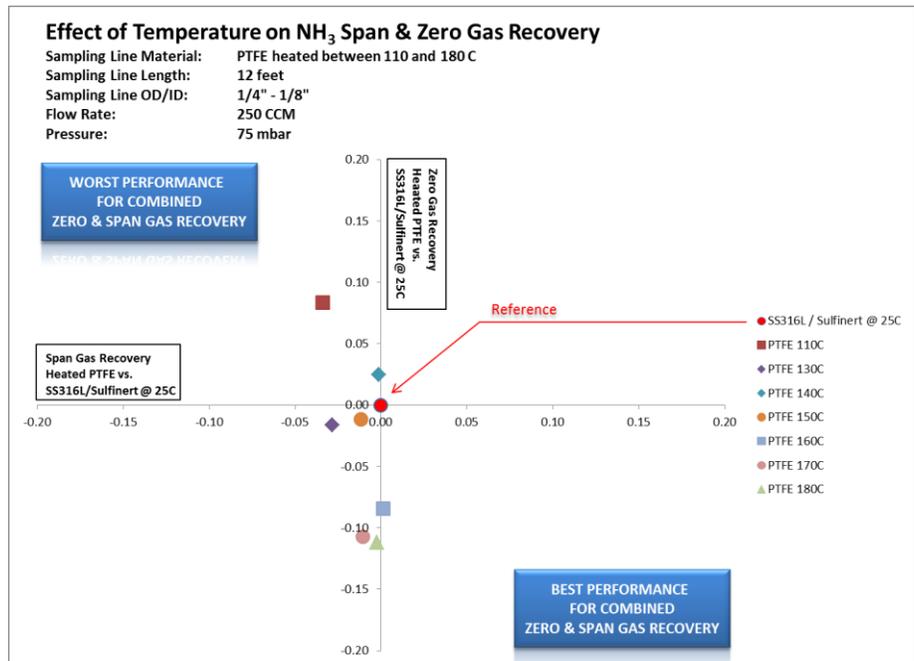


Fig. 5c: effect of temperature on NH<sub>3</sub> measurement system combined recovery rate and purge efficiency expressed as a function of the rise/fall time observed using a Sulfinert2000®-coated SS316L operated at room temperature.

Figure 5c attempts to simplify the selection process for an optimum temperature of operation of a PTFE line when comparing that performance to that of a Sulfinert2000®-coated sampling line operated at room temperature from the combined viewpoints of recovery rate and purge efficiency.

X-Axis carries 'Span Gas Recovery Rate' performance information and Y-Axis carries 'Zero Gas Recovery' (a.k.a. p[urge efficiency) performance information.

As no data point makes it into the upper- and lower right quadrant of the graph, we can report that heated PTFE sampling lines, regardless of the temperature of operation, do not improve on recovery rate of NH<sub>3</sub> when compared to the Sulfinert2000®-coated SS316L line.

However, it seems that, for temperatures above 140°C there is a very slight (up to 0.2 ppm) improvement in purge efficiency under the experimental thermodynamic conditions used when compared to the purge efficiency performance of a Sulfinert2000®-coating SS316L line operated at room temperature.

From these observations, it seems that:

- a PTFE line operated at high temperature (at least 140°C confirmed) is recommended to match the NH<sub>3</sub> recovery rate performance otherwise obtained using a Sulfinert2000®-coated SS316L sampling line operated at room temperature.
- A PTFE line heated @ 170-180°C seems to offer a slight advantage to a Sulfinert2000®-coated SS316L sampling line operated at room temperature in terms of purge efficiency. However, this advantage is very small (only 0.2 ppm improvement for a ca. 100 ppm range tested).

**EXPERIMENT 3**

**Analytical Performance Qualification of a SEMTECH® LASAR NH<sub>3</sub> Analyzer operated with a Sulfinert2000®-coated SS316L Sampling Line Operated at Room Temperature.**

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**Experimental:**

- A SEMTECH® LASAR was calibrated for the measurement of NH<sub>3</sub>.
- Analyzer operation conditions were:
  - Flow rate = 280 CCM
  - Sampling line = Sulfinert2000®-coated SS316L
  - Temperature of sampling line = ambient (ca. 22-25°C)
  - Gas cell temperature = 45°C
  - Data acquisition rate = 10 Hz
  - Data reporting rate = 1 Hz.
  - NH<sub>3</sub> bottle concentration = 103.4 ppm
- The 80-minute gas blender program used for data collection is described in figure 6. It consisted of the following sequential series of 2-minute steps:
  - 10 step downs
  - 10 steps up
  - 5 repeats of injection at 100% of span with dry N<sub>2</sub> in-between
  - 5 repeats of injection at 5% of span concentration with dry N<sub>2</sub> in-between.
- Data treatments:
  - 7-assay accuracy at span concentration.
  - 2-assay repeatability at all 10 levels of concentrations tested.
  - Combined ascending and descending linearity (including SEE accuracy calculation).
  - 12-assay repeatability, precision and bias @ zero.
  - 5-assay repeatability, precision and bias at 5% of span concentration tested.
  - 5-assay repeatability, precision and bias at 100% of span concentration tested.
  - Rise and fall times.

**Results:**

All results are reported in tables 2a-2f and in figures 6a-6d below. Analytical performance qualification criteria are derived from existing regulatory documents for other regulated gases.

**Table 2a: 7-assay SPAN ACCURACY**

Criteria			Measured		Status
%	Min ppm	Max ppm	ppm	%	
≤ 2% of pt.	101.332	105.468	103.415	-0.01%	PASS

**Table 2b: Repeatability AT ALL LEVELS**

Criteria			Measured		Status
%	Min ppm	Max ppm	ppm	%	
≤ 1% of pt. @ 100% of span	0.000	1.034	0.530	0.51%	PASS
≤ 1% of pt. @ 90% of span	0.000	0.931	0.528	0.57%	PASS
≤ 1% of pt. @ 80% of span	0.000	0.827	0.655	0.79%	PASS
≤ 1% of pt. @ 70% of span	0.000	0.724	0.486	0.67%	PASS
≤ 1% of pt. @ 60% of span	0.000	0.620	0.362	0.58%	PASS
≤ 1% of pt. @ 50% of span	0.000	0.517	0.290	0.56%	PASS
≤ 1% of pt. @ 40% of span	0.000	0.414	0.275	0.66%	PASS
≤ 1% of pt. @ 30% of span	0.000	0.310	0.166	0.53%	PASS
≤ 1% of pt. @ 20% of span	0.000	0.207	0.124	0.60%	PASS
≤ 1% of pt. @ 10% of span	0.000	0.103	0.062	0.60%	PASS
≤ 1% of max @ 0% of span	0.000	1.034	0.016	0.02%	PASS

**Table 2c: LINEARITY**

Criteria			Measured		Status
%	Min ppm	Max ppm	ppm	%	
$R2 \geq 0.998$	0.998	1.000	1.000	---	PASS
$0.99 < \text{slope} < 1.01$	0.990	1.010	0.996	---	PASS
Intercept ≤ 0.5% of max	0.303	0.517	0.303	0.29%	PASS
SEE ≤ 1% of max	0.000	1.034	0.496	0.48%	PASS

**Table 2d: 5-Assays Testing @ Zero**

Criteria			Measured		Status
%	Min ppm	Max ppm	ppm	%	
Repeatability ≤ 1% of max	0.000	1.034	0.026	0.03%	PASS
Precision ≤ 1% of max	0.000	1.034	0.218	0.21%	PASS
Bias ≤ 1% of max	-1.034	1.034	0.415	0.40%	PASS

**Table 2e: 5-Assays Testing @ 5% of span concentration tested**

Criteria			Measured		Status
%	Min ppm	Max ppm	ppm	%	
Repeatability ≤ 1% of max	0.000	0.052	0.051	0.05%	PASS
Precision ≤ 1% of max	0.000	0.052	0.036	0.03%	PASS
Bias ≤ 1% of max	-2.068	2.068	0.090	0.09%	PASS

**Table 2f: 5-Assays Testing @ 100% of span concentration tested**

Criteria			Measured		Status
%	Min ppm	Max ppm	ppm	%	
Repeatability ≤ 1% of max	0.000	1.034	0.577	0.56%	PASS
Precision ≤ 1% of max	0.000	1.034	0.166	0.16%	PASS
Bias ≤ 1% of max	-2.068	2.068	0.277	0.27%	PASS

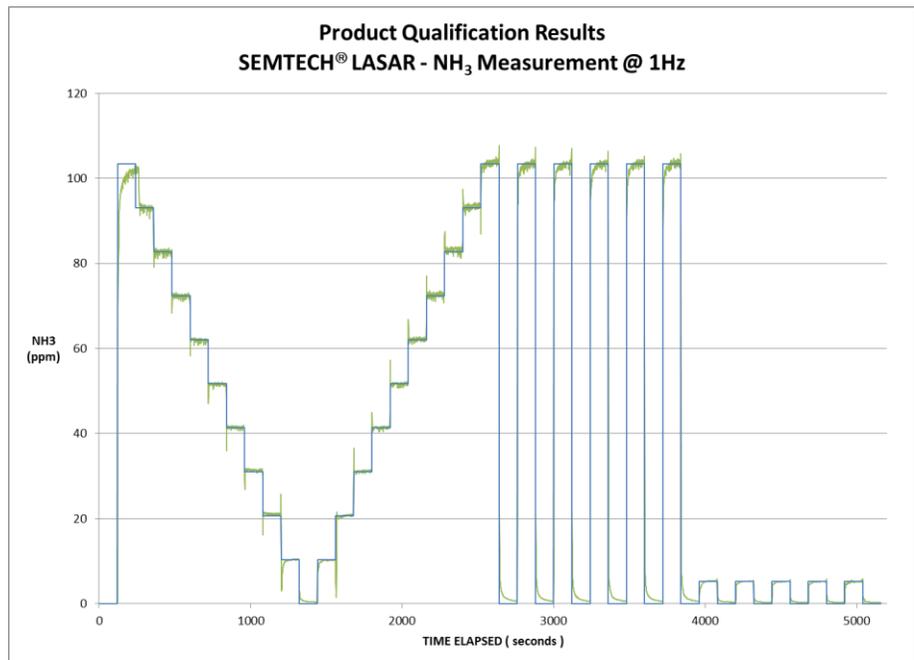


Fig. 6a: Analytical performance testing profile for qualification of SEMTECH® LASAR NH<sub>3</sub> analyzer used with a 3-meter Sulfinert2000®-coated SS316L sampling line operated at room temperature. Gas blender set point values as a function of time plotted in blue. Actual NH<sub>3</sub> measurement @ 1 Hz plotted in green.

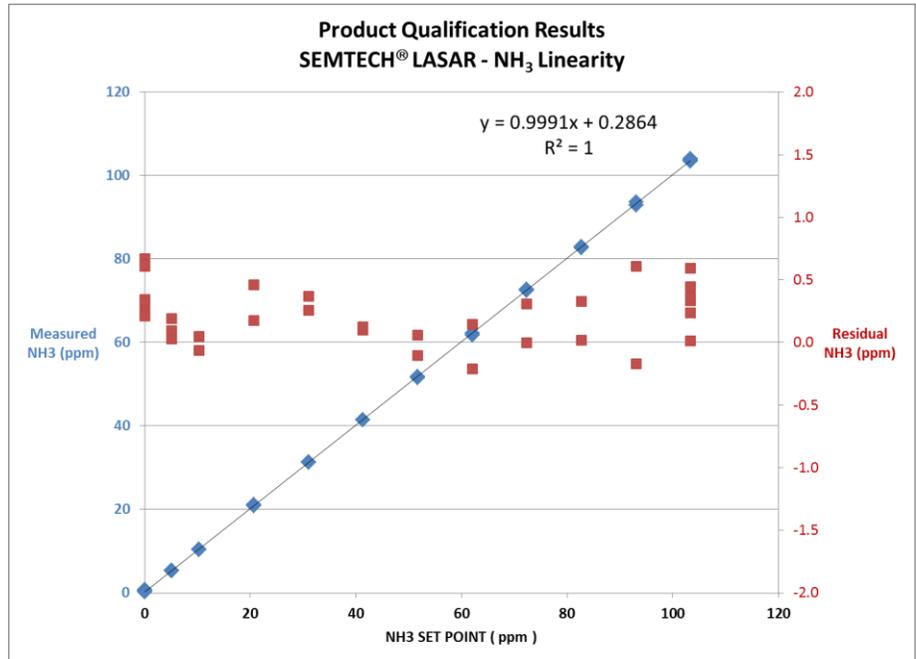


Fig. 6b: Analytical performance testing profile for qualification of SEMTECH® LASAR. Linearity test results. Average bias of approximately 0.3 ppm is observed.

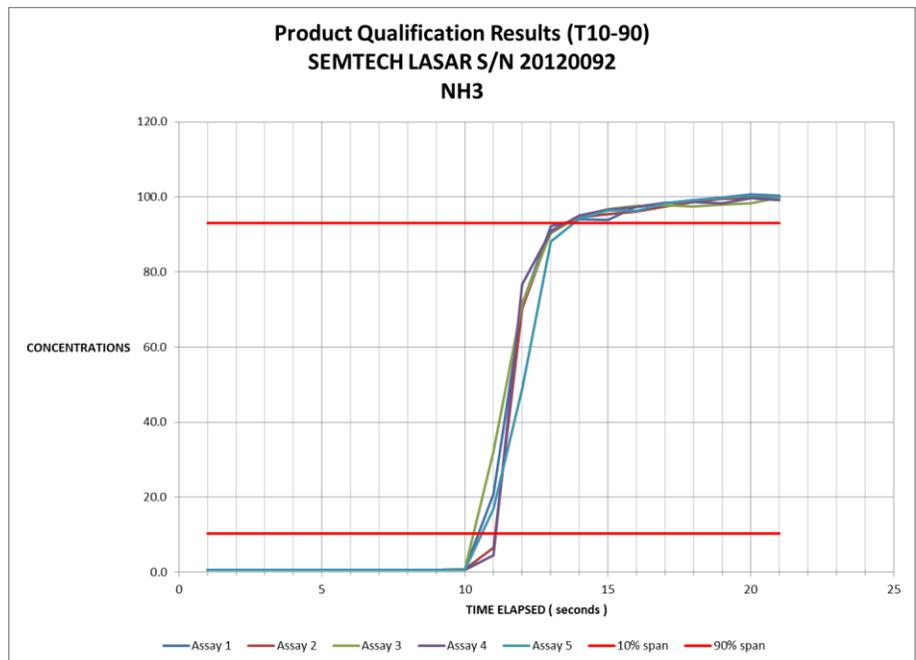


Fig. 6c: Rise time test results. Average  $T_{10-90}$  of approximately 2.5 seconds using 175 micron diameter critical orifice enabling 260 CMM flow rate at 75 mbar sampling line pressure. This rise time can be further improved when using a 200 micron diameter critical orifice enabling 340 CMM flow rate (a 131% increase) under the same pressure conditions.

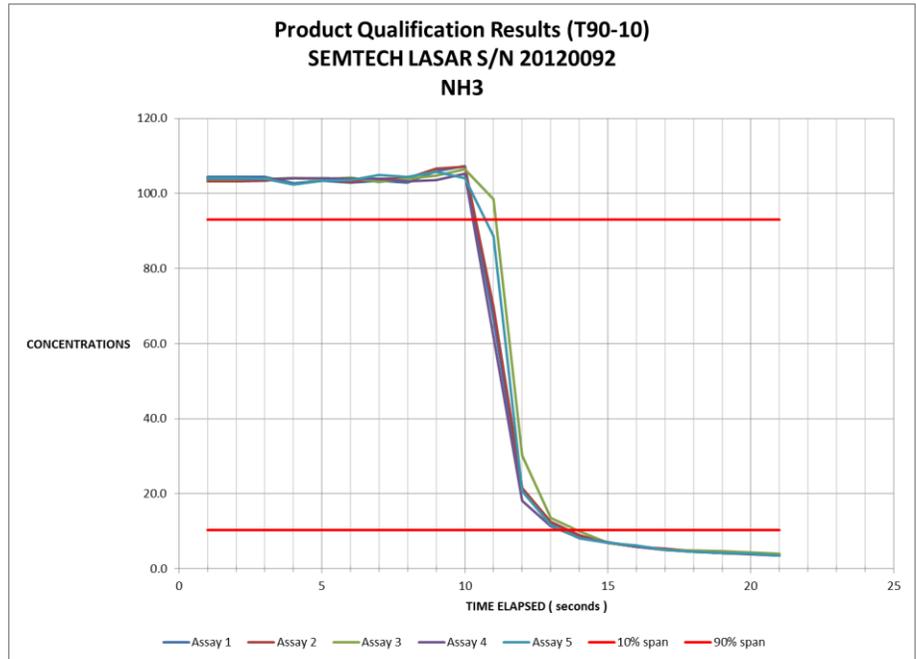


Fig. 6d: Fall time test results. Average  $T_{100-10}$  of approximately 2.5 seconds using 175 micron diameter critical orifice enabling 260 CMM flow rate at 75 mbar sampling line pressure. This fall time can be further improved when using a 200 micron diameter critical orifice enabling 340 CMM flow rate (a 131% increase) under the same pressure conditions.

## CONCLUSIONS

Results of test 1 unequivocally shows that, at equivalent operating conditions of temperature, pressure and flow rate, Sulfinert2000®-coated SS316L sampling lines offer the fastest response and recovery rates for the measurement of NH<sub>3</sub> using an extractive spectrophotometric method when compared to PTFE and standard SS316L sampling lines.

Results of test 2 suggest that equivalent recovery rates and marginally improved rise times may be obtained if substituting a PTFE sampling heated to at least 160°C (preferably 180°C) to the proposed Sulfinert2000®-coated SS316L sampling line operated at room temperature. However, from a sampling accuracy viewpoint, one must consider the highly increase reaction rates of transformative chemical reactions that may occur in the sampling line between NH<sub>3</sub> and other chemical species present; full qualification of a high-temperature heated PTFE sampling line from a sampling accuracy would require a formal quantification of the errors generated by these parasite chemical reactions, the subject of another study.

Results of test 3 show that the use Sulfinert2000®-coated SS316L sampling lines operated at room temperature in conjunction with an extractive spectrophotometer enables analytical performance qualification of the system as tested against accuracy, linearity, precision, repeatability and response times consistent with those currently enacted for the measurement of other regulated pollutants in the emissions of internal combustion engines, thus suggesting the viability of the sampling method within the scope of a potential regulation pertaining to the measurement of NH<sub>3</sub> is such emissions.

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**APPENDIX 1 – Individual Experimental Results obtained during Test 2.**

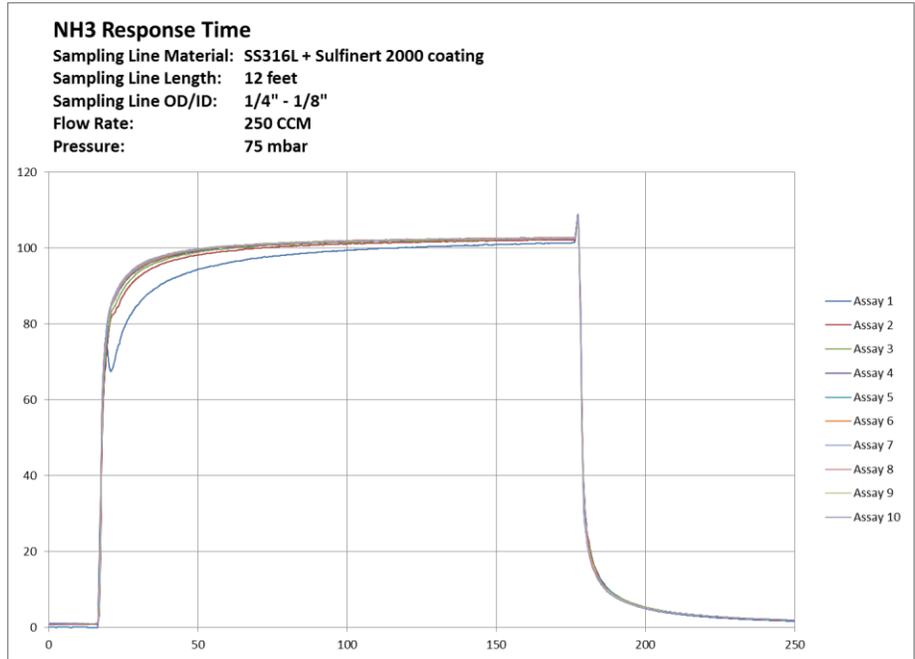


Figure A-1: NH<sub>3</sub> response time using Sulfinert2000®-coated SS316L sampling line operated at room temperature.

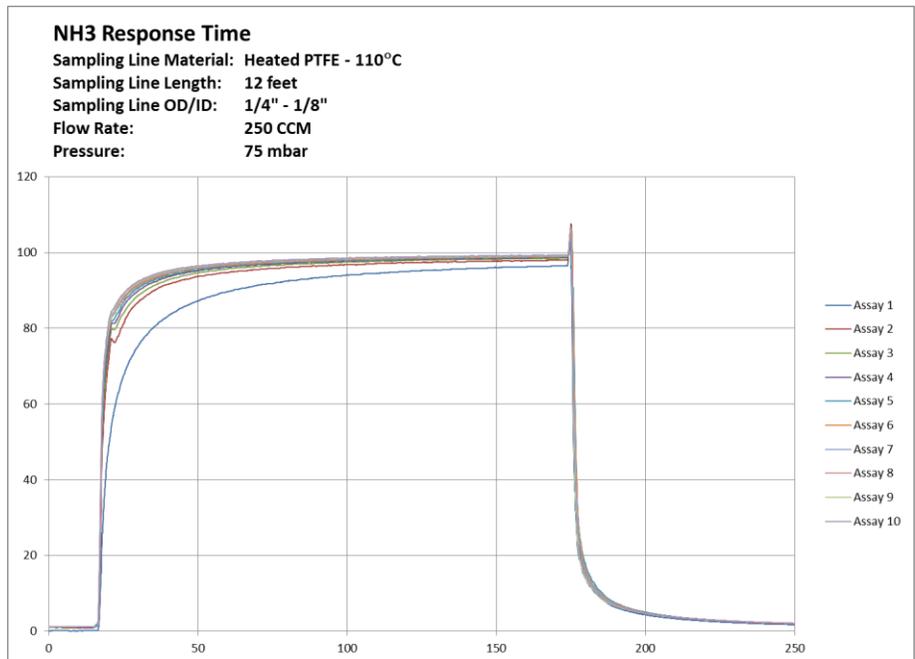


Figure A-2: NH<sub>3</sub> response time using PTFE sampling line heated @ 110°C.

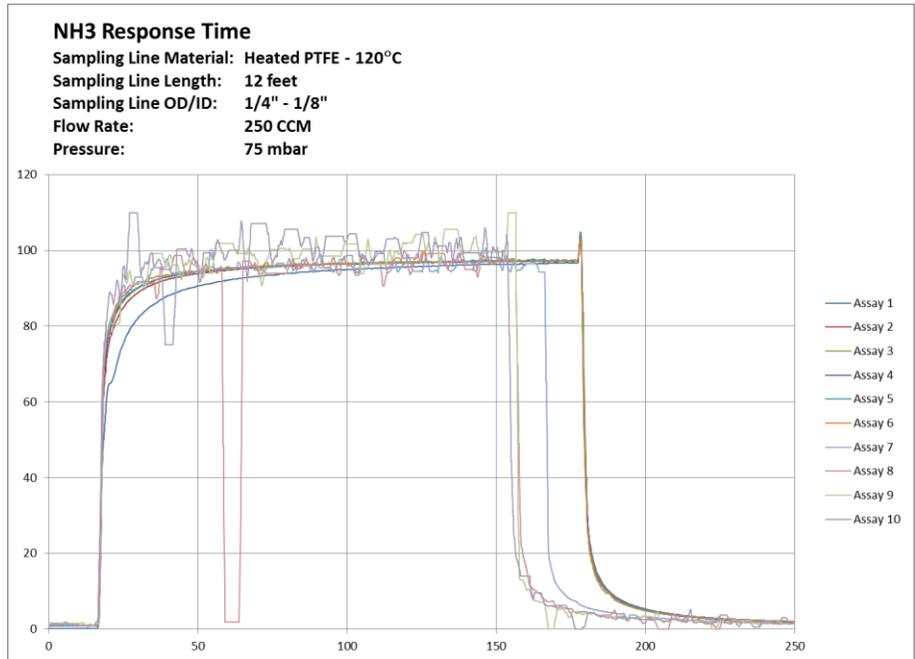


Figure A-3: NH<sub>3</sub> response time using PTFE sampling line heated @ 120°C.  
Problems with the automated gas divider occurred during this run.  
These set of data points are not taken into consideration in the study.

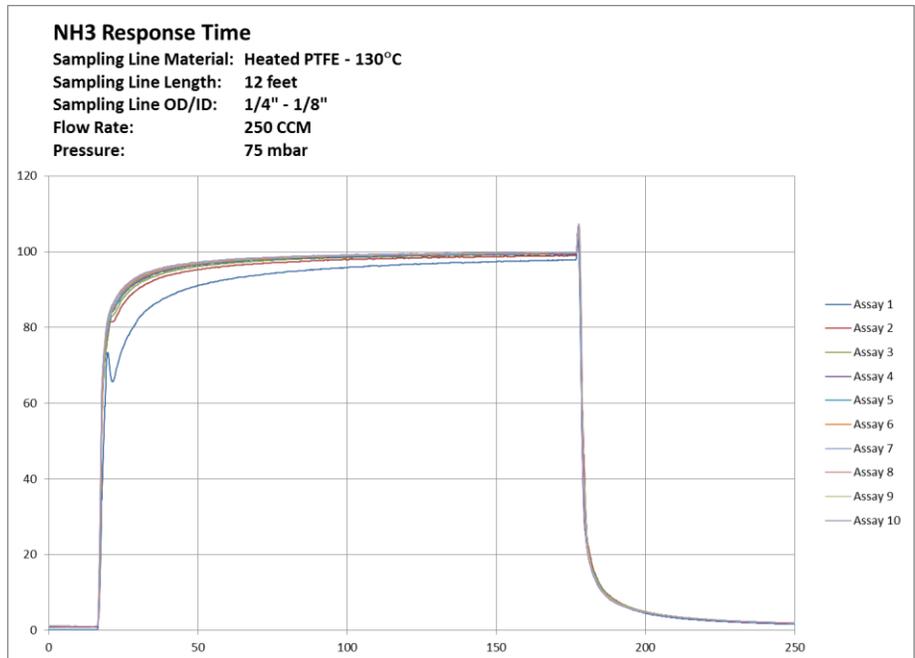


Figure A-4: NH<sub>3</sub> response time using PTFE sampling line heated @ 130°C.

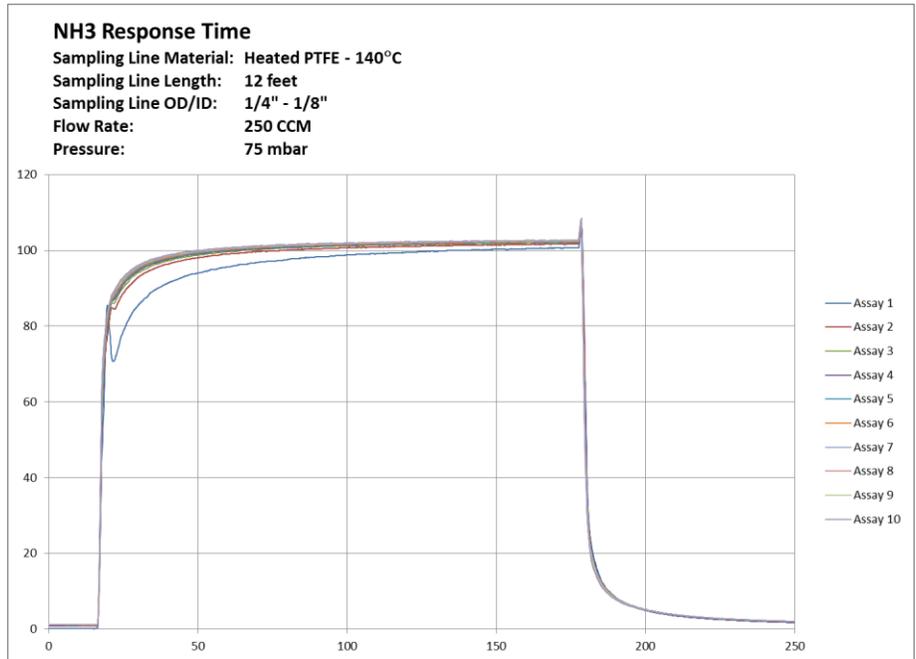


Figure A-5: NH<sub>3</sub> response time using PTFE sampling line heated @ 140°C.

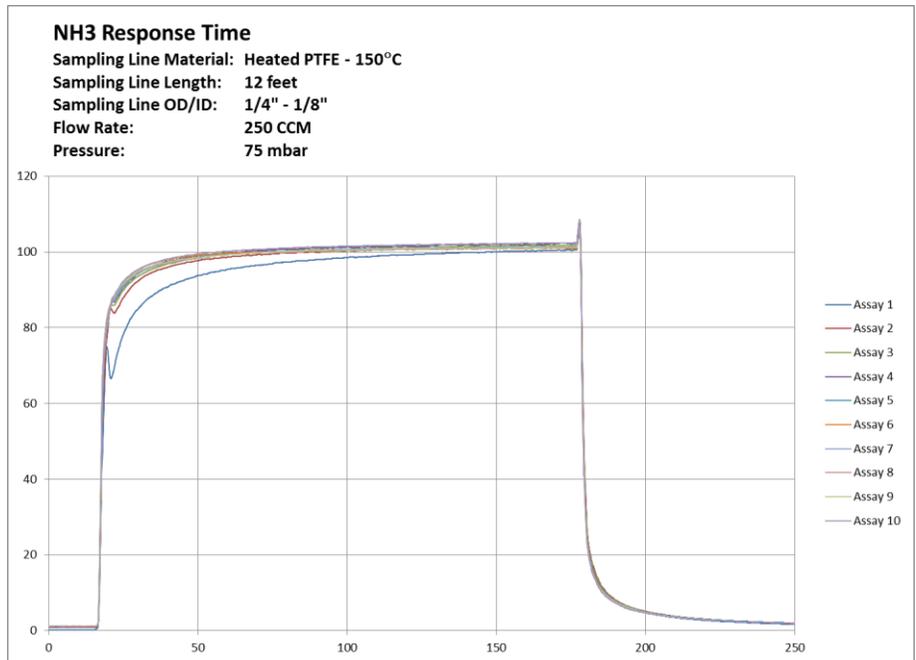


Figure A-6: NH<sub>3</sub> response time using PTFE sampling line heated @ 150°C.

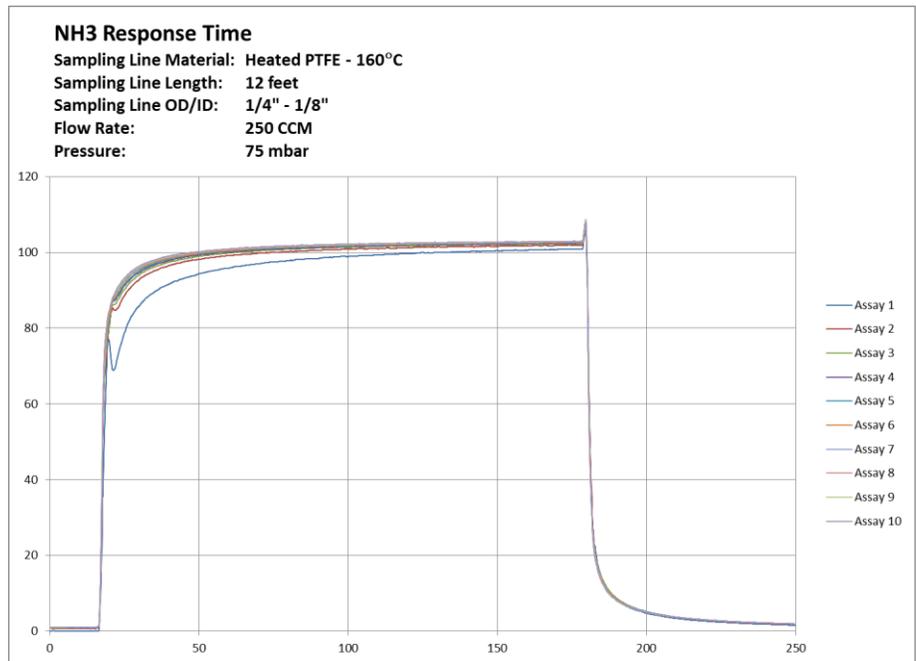


Figure A-7: NH<sub>3</sub> response time using PTFE sampling line heated @ 160°C.

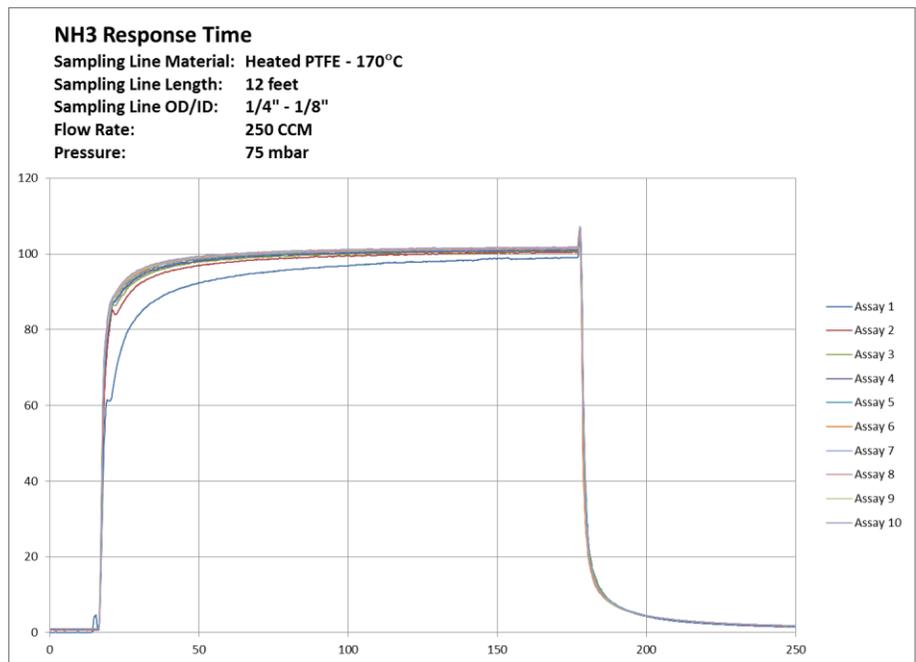


Figure A-8: NH<sub>3</sub> response time using PTFE sampling line heated @ 170°C.

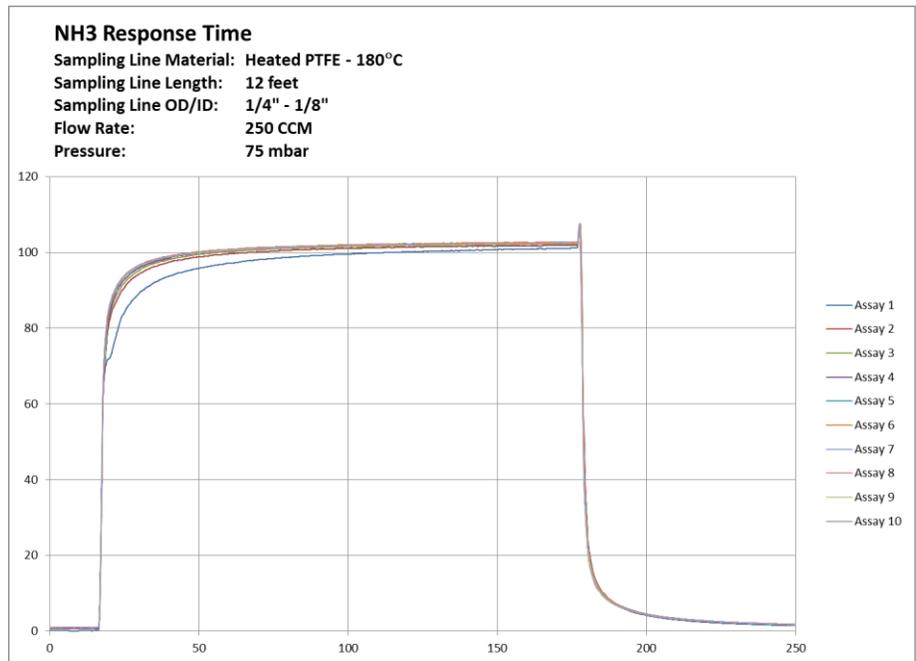


Figure A-9: NH<sub>3</sub> response time using PTFE sampling line heated @ 180°C.

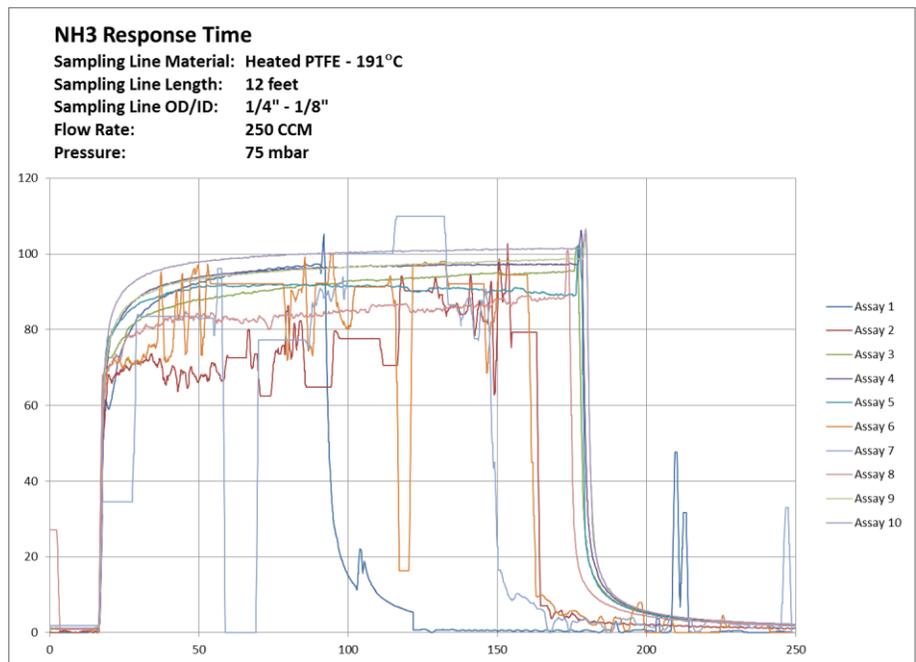


Figure A-10: NH<sub>3</sub> response time using PTFE sampling line heated @ 191°C.

Problems with the automated gas divider occurred during this run.  
These set of data points are not taken into consideration in the study.