



**CALIFORNIA
ENERGY
COMMISSION**

**Quantification Of Uncertainties In
Continuous Measurement Systems
For Low-NO_x Emissions From
Stationary Sources**

CONSULTANT REPORT

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Preface

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace.

The PIER Program, managed by the California Energy Commission (Commission), annually awards up to \$62 million to conduct the most promising public interest energy research by partnering with Research, Development, and Demonstration (RD&D) organizations, including individuals, businesses, utilities, and public or private research institutions.

PIER funding efforts are focused on the following six RD&D program areas:

- Buildings End-Use Energy Efficiency
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Energy Systems Integration.

What follows is the final report for the “Quantification of Uncertainties in Continuous Measurement Systems for Low-NO_x Emissions from stationary Sources”, Contract Number: 500-97-032, conducted by University of California, Riverside, Bourns College of Engineering-Center for Environmental Research and Technology. The report is entitled “Quantification of Uncertainties in Continuous Measurement Systems for Low-NO_x Emissions from stationary Sources.” This project contributes to the Energy-Related Environmental Research program.

For more information on the PIER Program, please visit the Commission's Web site at: <http://www.energy.ca.gov/research/index.html> or contact the Commission's Publications Unit at 916-654-5200.

Executive Summary

The University of California, Riverside, Bourns College of Engineering-Center for Environmental Research and Technology (CE-CERT), an independent laboratory, conducted a study to quantify sources of error in NO_x measurement methods applied to low-NO_x and new-technology emission sources. The program addressed potential biases resulting from sampling system materials, temperature effects, moisture removal systems, NO₂ converter strategies, and the presence of ammonia in sample streams.

The study began with a review of previous work in low NO_x measurement. A test program was then executed to assess the accuracy and precision of currently employed methods and equipment to measure NO_x emissions from new and near-term power generation processes for stationary sources.

Objectives

The laboratory testing objectives were:

- Quantification of NO_x measurement biases in sample handling and conditioning of existing measurement systems under wet and dry conditions.
- Quantification of interference caused by ammonia at a variety of concentrations and moisture conditions.

Six different types of sample conditioners were evaluated in this test program: a permeation dryer, a combination ambient condenser/permeation dryer, a thermoelectric chiller, a refrigerated coil-type condenser, and a Method 5-style sampling train with impingers in an ice bath, and a dilution extractive probe.

Three different types of sample lines were also evaluated in this test program: PFA Teflon, 316L stainless steel, and 316L Silcosteel® (stainless steel with a thin glass lining). The lines were evaluated at three different temperatures (25°C, 107°C, and 175°C).

Three different types of alternative sampling systems were evaluated in this test program: a system with an up-front NO₂ to NO converter followed by a thermoelectric chiller, a hot/wet molybdate carbon converter and analyzer with no moisture knockout, and a dilution extractive system using a molybdate carbon converter.

Outcomes

The following outcomes were observed.

Sample Conditioners

- No ammonia was detected at the analyzer sampling manifold throughout testing of all sample conditioners, except for a slight amount detected at a few conditions.
- Use of the sample conditioning systems resulted in measured NO_x values that were lower than input values, except for a few test conditions. The greatest differences (approximately -10 percent to -25 percent of input concentration) occurred at the lowest NO_x input conditions. Losses measured at all other conditions (>2 ppm input NO_x) were all less than 10 percent. Of all sample conditioning systems tested, the permeation dryer and thermoelectric chiller resulted in the greatest differences.

- No differences were observed with any sample conditioning system due to water input. Test conditions using 6 percent water and 13 percent water input were statistically no different than dry simulated exhaust with respect to NO_x measurement. Results did show approximately 30 percent increased loss (relative to baseline wet exhaust case) for all conditioning systems tested when ammonia was added to the wet sample stream.

Sample Lines

- In combination with the reference sample conditioner, average losses through the sample lines were approximately 20 percent for the low NO_x (0.2 ppm NO, 0.2 ppm NO₂) conditions, 5 percent for the conditions with 1 ppm/1 ppm and 4.7 ppm/4.7 ppm NO/NO₂ inputs, and 2 percent for the 9 ppm/1 ppm NO/NO₂ conditions.
- Average losses through the reference sample conditioner alone for the same three sets of conditions were 23 percent, 10 percent, and 7 percent, respectively. It was concluded that the vast majority of NO_x losses in measurement systems occur in the sample conditioning systems, and not the sample lines.
- There were no statistical differences observed between any of the sample line test conditions, regardless of material used or operating temperature. The only exception was that, in the presence of ammonia and water, NO_x losses increased (for the lowest NO_x input) in the stainless steel line operating at 175°C.

Alternative Sampling Systems

- Overall, the measured differences relative to the input NO_x concentrations for these three systems (2 percent to 35 percent) were higher than those observed in the traditional sampling systems (2 percent to 20 percent) under the tested conditions. Furthermore, these differences changed more dramatically than the traditional systems with changing conditions, in some cases shifting results from a high positive bias to a high negative bias with a slight change in input gas composition.
- For the analyzer with the hot/wet vitreous carbon converter, results showed an increasing negative bias as a function of NO₂ input concentration (from ~20 percent at 0.2 ppm NO₂ input to ~30 percent at 4.7 ppm NO₂ input).
- For the analyzer with the hot/wet molybdate carbon converter, results showed that the addition of water to the sample stream resulted in a positive bias in all cases, and increased as a function of water input (~3 percent average bias for dry simulated exhaust, ~7 percent average bias for wet [6 percent H₂O] simulated exhaust, and ~19 percent bias for wet [13 percent H₂O] simulated exhaust).
- The addition of ammonia to the sample stream resulted in a negative effect on NO_x readings at low concentrations, but a positive effect on NO_x readings at higher concentrations. In general, the percentage absolute error increased with increasing NO_x concentrations.
- For the analyzer using the dilution extraction probe, there was a consistent negative bias on measured versus input NO_x concentrations. This could be a result of dilution error, possibly from an incorrect calibration of the dilution airflow control and/or sample flow control systems. Results indicated an increasing absolute bias (negative) with increasing NO₂ concentrations.

Additional testing was performed to more conclusively determine the effects of potential ammonia concentrations in combustion sources with low concentrations of NO_x. Once again, synthetically-prepared mixtures of pure gases and simulated exhaust gases were generated and passed through various sample lines and sample conditioning systems into the chemiluminescent analyzers with various NO₂ to NO converters.

Conclusions

Several significant conclusions were drawn from these experiments.

- Neither the sample line material/temperature nor choice of sample conditioner had a significant effect on the ammonia detected when CO₂ was not present. The exception was the glass impingers in an ice bath, which removed more ammonia than the other systems. Even in this case, however, the majority of ammonia penetrated through to the converters. When CO₂ was included, virtually no ammonia could be measured. Some ammonia was detected at the 6 percent water input case, but very little of the input in all test cases was detected when CO₂ and water were both present.
- An ammonia accumulation effect was observed in the stainless steel NO_x converter. This phenomenon was not observed in any other converter, including the high temperature stainless steel converter associated with the ammonia analyzer. The effect was also not present in the stainless steel heated sampling line, perhaps due to its relatively new (unoxidized) condition.
- When using synthetic exhaust, neither the sample line material/temperature affected the ammonia nor NO_x measured. Both PFA and stainless steel sampling lines at 107°C behaved in a similar manner for both ammonia and NO_x penetration. In all cases, the molybdenum-based converter showed no response to ammonia.
- In addition to the finding of ammonia losses in wet sample streams in the presence of CO₂, there are interactions between NO and NO₂ with ammonia that occur at elevated temperatures, leading to NO_x losses in the sampling lines and conditioning systems.

Benefits to California

Accurate and precise measurements of NO_x emissions from new and near-term power generation processes are critical for determining compliance as well as offsets for NO_x credit trading programs. Many new plants use SCR for NO_x control. Efficient and cost-effective plant operation (through feedback control) requires NO_x monitoring at inlet to the SCR, and NO_x/NH₃ monitoring at the outlet of the SCR. These monitors, therefore, must be accurate, precise, and durable. The ability to quantify sources of error in NO_x measurement methods in application to low-NO_x and new-technology emission sources directly benefits the rate payer of California by allowing the accuracy and precision necessary to determine compliance with air quality and emissions rules and regulations.

Recommendations

The following future actions and studies are recommended.

- Develop and implement measurement systems with low enough analytical ranges to meet protocol requirements of sample concentrations of at least 20% of sample range.

- Determine the exact nature of the interactions between NO and NO₂ with ammonia that occur at elevated temperatures that leading to NO_x losses in the stainless steel sampling line.
- Conduct long term sampling (greater than two hours) for each condition to obtain consistent readings when ammonia is present in the sample stream and which would reveal the exact nature of ammonia accumulation and NO_x measurement effects.
- Evaluate ammonia losses in sample streams in the presence of CO₂. A potential test matrix would include simulated sample streams with multiple CO₂ and ammonia concentrations. Each test point would be evaluated with and without water vapor present.

Abstract

The University of California, Riverside, Bourns College of Engineering-Center for Environmental Research and Technology (CE-CERT), an independent laboratory, conducted a study to quantify sources of error in nitrogen oxides (NO_x) measurement methods in application to low-NO_x and new-technology emission sources. The program addressed potential biases resulting from sampling system materials, temperature effects, moisture removal systems, nitrogen dioxide (NO₂) converter strategies, and presence of ammonia in sample streams.

The study began with a review of previous work in low NO_x measurement. A test program was then executed to assess the accuracy and precision of currently employed methods and equipment to measure NO_x emissions from new and near-term power generation processes for stationary sources.

Several significant conclusions were drawn from the study. In general, accurate NO_x measurements were demonstrated using all sample conditioning systems and sample lines for NO_x sample concentrations at or above 2 ppm. At concentrations below 2 ppm, there were considerable differences between sampling systems, and a much higher degree of variability in results.

An interesting phenomenon was observed with regard to the presence of ammonia in sample streams. Without carbon dioxide (CO₂) present, ammonia was detected in majority of quantities input through all sample line materials/temperatures, and sample conditioning systems. Neither the sample line material/temperature nor choice of sample conditioner had a significant effect on the ammonia detected when CO₂ was not present. When CO₂ was added to the sample stream, virtually no ammonia could be measured. An ammonia accumulation effect was observed in the stainless steel NO_x converter, suggesting that ammonia is accumulated and subsequently converted to NO over a relatively long period of time (greater than one hour). This phenomenon was not observed in any other converter, including the high-temperature stainless steel converter associated with the ammonia analyzer.

The study concluded that ammonia is removed from wet sample streams in the presence of CO₂. Furthermore, the study suggests interactions between NO and NO₂ with ammonia that occur at elevated temperatures, leading to NO_x losses in the sampling lines and conditioning systems. Further study is recommended to determine the exact nature of these interactions. Results also show that long-term sampling (greater than two hours) for each condition may be required to obtain consistent readings when ammonia is present in the sample stream.

1.0 Introduction

A survey conducted in response to a 1999 continuous emission monitoring system (CEMS) users group¹ direction identified three main concerns in low-NO_x measurement:

1. Lack of low-level protocol span gases.
2. Precision of the method and instrumentation at low levels.
3. Instrumental ammonia interference.

Five CEMS operators (with sub-5 ppm NO_x concentrations) and one source testing company responded to the survey. Operators questioned the accuracy and precision of existing measurement technology with monitoring new ultra-low emission (<5 ppm NO_x @ 15 percent O₂) combustion systems. Comments from the users group also concerned potential measurement problems during dynamic operation (i.e. start-up or load shifting) and operation near regulatory limits. Most turbine units operate within 25 percent of permitted levels, while some operate within 10 percent.

Recently, operators of low-NO_x facilities have reported difficulty in passing relative accuracy (RATA) tests. The ±20 percent pass criteria are within traditional instrument precision at these levels (3 ppm). Most operators consider the existing RATA protocol to be restrictive for ultra-low sources. Additional concerns relate to the availability of low-level EPA Protocol 1 span gas (and associated increase in costs compared with traditional blends).

Power plants being reviewed for licensing are expected to have concentrations at the ppm level and below, with higher NO₂ to NO_x ratios than historical emissions, and often utilizing ammonia injection as an after treatment technology to achieve these very low concentrations. Some current monitoring methods may easily have an uncertainty on the same order as the concentration of the source. New analyzers, converters, and sample conditioning technologies are being developed to make accurate measurements at these low concentrations. The accuracy of these systems to measure such low concentrations has not been fully evaluated.

1.1 Background

The University of California, Riverside, Bourns College of Engineering-Center for Environmental Research and Technology (CE-CERT), an independent laboratory, conducted a study to quantify sources of error in nitrogen oxides (NO_x) measurement methods in application to low-NO_x and new-technology emission sources. The program addressed potential biases resulting from sampling system materials, temperature effects, moisture removal systems, nitrogen dioxide (NO₂) converter strategies, and presence of ammonia in sample streams.

The study began with a review of previous work in low NO_x measurement. A test program was then executed to assess the accuracy and precision of currently employed methods and equipment to measure NO_x emissions from new and near-term power generation processes for stationary sources. The specific laboratory testing objectives were:

- Quantification of NO_x measurement biases in sample handling and conditioning of existing measurement systems under wet and dry conditions.
- Quantification of interference caused by ammonia at a variety of concentrations and moisture conditions.

Several significant conclusions were drawn from the study. In general, accurate NO_x measurements were demonstrated using all sample conditioning systems and sample lines for NO_x sample concentrations at or above 2 ppm. At concentrations below 2 ppm, there were considerable differences between sampling systems, and a much higher degree of variability in results.

An interesting phenomenon was observed with regard to the presence of ammonia in sample streams. Without carbon dioxide (CO₂) present, ammonia was detected in similar concentrations to those input through all sample line materials/temperatures, and sample conditioning systems. Neither the sample line material/temperature nor choice of sample conditioner had a significant effect on the ammonia detected when CO₂ was not present. When CO₂ was added to the sample stream, virtually no ammonia could be measured. An ammonia accumulation effect was observed in the stainless steel NO_x converter, suggesting that ammonia is accumulated and subsequently converted to NO over a relatively long period of time (>1 hr). This phenomenon was not observed in any other converter, including the high-temperature stainless steel converter associated with the ammonia analyzer.

The study concluded that ammonia is removed from wet sample streams in the presence of CO₂. Furthermore, the study suggests interactions between NO and/or NO₂ with ammonia that occur at elevated temperatures, leading to NO_x losses in the sampling lines and conditioning systems. Further study is recommended to determine the exact nature of these interactions. Results also show that long-term sampling (greater than 2 hours) for each condition may be required to obtain consistent readings when ammonia is present in the sample stream.

Objectives

The laboratory testing objectives were:

- Quantification of NO_x measurement biases in sample handling and conditioning of existing measurement systems under wet and dry conditions.

- Quantification of interference caused by ammonia at a variety of concentrations and moisture conditions.

Six different types of sample conditioners were evaluated in this test program: a permeation dryer, a combination ambient condenser/permeation dryer, a thermoelectric chiller, a refrigerated coil-type condenser, and a Method 5-style sampling train with impingers in an ice bath, and a dilution extractive probe.

1.2 Discussion

NO_x formation in boilers and turbines occurs as a function of temperature, residence time, excess air, N₂/O₂ concentrations, and extent of mixing.³ In turbines, NO_x formation is minimized through lean primary zone (premixed) operation resulting in lower flame temperatures, reduced combustion zone volume (minimizing residence time), increased liner pressure drops (increased turbulence and mixing), and by using water or steam injection (lower flame temperature). In boilers, NO_x formation is minimized through combustion zone cooling (e.g. flue gas recirculation [FGR] to lower flame temperature), low-NO_x burners, and staged combustion (to reduce temperatures and reduce available oxygen). None of the primary combustion techniques alone, however, results in NO_x levels below limits currently set by regulatory agencies.³ Many current and proposed gas turbine plants use advanced lean burn (DLN) combustion systems. At reduced loads and reduced combustion efficiencies, the NO₂ component increases. Some manufacturers and researchers have asserted that newer turbines with single-digit NO_x concentrations may emit from 50 percent to 90 percent of the total NO_x as NO₂.⁴ Others claim that the NO₂ component is not that substantial.

Accurate and precise measurements are critical for determining compliance as well as offsets for NO_x credit trading programs. Many new plants use SCR for NO_x control. In the SCR process, ammonia is injected directly into the flue gas. Reduction of NO_x occurs in a separate reactor vessel containing a reduction catalyst maintained at 232-399 °C. The catalyst is usually a mixture of titanium dioxide, vanadium pentoxide, and tungsten dioxide. In the presence of ammonia, both NO and NO₂ are reduced to nitrogen and water.³ The mass flow rate of ammonia injected must be sufficient to achieve required NO_x reduction, but small enough to prevent ammonia slip (as maximum allowable NH₃ slip is typically listed as a permit condition). Exact stoichiometry of NH₃/NO_x is difficult to achieve due to uneven flow distribution, temperature stratification, and monitor/process response times. As ammonia slip is commonly regulated, it is advantageous to monitor with CEMS. Efficient and cost-effective plant operation (through feedback control) requires NO_x monitoring at inlet to the SCR, and NO_x/NH₃ monitoring at the outlet of the SCR. These monitors, therefore, must be accurate, precise, and durable.

SCR systems are used in a wide range of gas-fired applications. They operate in environments with temperatures up to 427 °C for boilers, up to 649 °C for turbines, inlet NO_x concentrations from 15 to 1000 ppmvd, outlet concentrations down to 0.5 ppmvd, Outlet ammonia concentration limits down to 6 ppmvd, SO₂ concentrations between 0 and 2 ppmvd, and PM (dust) concentrations up to 0.02 gr/dscf³.

Large gas-fired boilers and turbines generally have large cross-sectional flue gas duct arrangements and unique geometries (leading to eddies, stratification, and cyclonic flow). For representative sampling of flow-sensitive components, some recommend a multi-point strategy based on flow mapping.³ Sampling and analytical strategies for CEMs must also take into account the presence of SO₂ and NH₃. In the presence of SO₂, temperatures below 268 °C can result in sulfate deposits in the sampling system. The concentration of mercaptans in natural gas used for odorizing does not pose a problem, provided that the sample train is kept at elevated temperatures.

As flue gas levels decrease across the SCR reducing catalyst, the NO₂ to NO ratio grows, increasing the importance of the moisture removal and converter components of the sampling system.³ Critical elements include proper sample path heating and moisture removal, and minimization of sample line length (to minimize response time, maintenance, and potential adsorption/desorption). For ammonia measurement, the most common technique is chemiluminescence with a high-temperature stainless steel converter at or near the sample probe.³

Chemical transformation of nitrogen oxides in probes and sample lines are of three general types: oxidation of NO to NO₂ (total NO_x conserved), NO₂ reduction to NO (NO_x conserved), and complete NO/NO₂ reduction to N₂ (NO_x not conserved).⁴ Additional reactions can create NO_x (e.g. oxidation of NH₃). NO₂ to NO reductions can occur in stainless steel sampling lines at temperatures of 200 °C and above (consistent with studies of stainless steel NO₂ converters). One study concluded that total NO_x is conserved in silica and 316 stainless steel sample probes for temperature ranges of 25-to 200 °C and residence time of ½ second in the presence of CO, H₂ or O₂. The study also found that, in the presence of H₂, NO_x is removed in stainless steel probes above 200 °C and in silica probes above 300°C.⁵

Measuring NO₂ is the primary problem when quantifying total NO_x concentrations. This compound is highly soluble in water, so methods that remove water from the sampled exhaust stream need to be carefully evaluated to determine that a significant amount of NO₂ is not also removed. This was less of a problem in the past, when NO₂ constituted only a few percent of the total NO_x emission concentrations. A critical step in proper sample conditioning is to prevent contact of gaseous NO₂ with condensed water.⁶ One suggested sampling system to minimize biases includes the following:

1. Water-cooled stainless steel phase discrimination probe or quartz probe.
2. Heated glass filter (110 °C) with quartz housing.
3. Heated Teflon line (110 °C).
4. Heated pump (93 °C) with Teflon or Viton head.
5. Upstream NO₂ to NO converter.
6. Miniature spiral stainless steel water trap (minimal residence time).
7. Shortest sample line lengths possible.⁵

CEMS use three types of sample acquisition techniques: dilution-extractive, direct extractive, and in-situ. Some CEM sampling systems use the dilution-extractive technique. This allows for measurement of concentrations on a wet basis. As flow measurements are made on a wet basis, it is convenient for calculating mass emission rates from wet concentration measurements. Also, CO₂ is measured as the diluent, rather than O₂, eliminating the need for an additional instrument. The two types of dilution-extractive probes are in-stack and out-of-stack. Most commonly used are the in-stack dilution-extractive probes, where dry filtered air is introduced in the sample stream at the probe. Dilution ratios typically range from 50:1 to 300:1 (100:1 is most common). The sample gas flow rates from the various probes range from 50 to 300 ml/minute. Two criteria are used to determine the proper dilution ratio: 1) the analyzer span

range must correspond to the diluted sample gas concentration, and 2) the ratio must be selected to ensure that no condensation occurs in the sample line at the lowest possible ambient temperature.

Direct extractive systems are used in the majority of CEMS used in gas turbine applications. The challenge with these systems is the difficulty in extracting, transporting, and conditioning a hot, wet, and particulate-laden flue gas for analysis. The two types of direct extractive systems are classified as “cold/dry” and “hot/wet.” The “cold/dry” systems consist of a probe, PM filter, heated sample line, moisture removal, and analyzers.⁶ The “hot/wet” systems forgo the moisture removal component and directly measure emissions concentrations on a wet basis.

The most common method of ammonia analysis consists of high temperature conversion of ammonia to NO, followed by chemiluminescent detection. Ammonia concentrations are determined as the difference between the above analysis and the CEMs direct NO_x measurement. If NO_x concentrations are kept constant at the SCR outlet, ammonia concentrations will increase over time (as the reduction catalyst degrades.² Other current or near-term instruments include direct measurement with tunable diode laser (TDL) detection, ion mobility spectroscopy (IMS), and electrochemical detection.²

Another issue resulting from increasingly lower stack concentrations is instrument scale factors. For example, measurements made below 5 ppm on a scale of 0-25 ppm are below 20 percent of scale. This can reduce the accuracy of the readings and result in a measurement uncertainty. Some suggest this uncertainty can exceed 25 percent.³

Chemiluminescent analyzers are usually calibrated with a blend of NO in an N₂ balance. When sampling from combustion systems, additional species are introduced, including H₂O, CO₂, CO, O₂, and H₂. Under certain circumstances, the composition of the gas mixture can affect the indicated measurement of NO due to differences in third body quenching reactions between the calibration gas and the sample gas. An example of third body quenching is given using a simulated gas-fired power plant is given. The presence of water vapor at 17 percent by volume leads to an NO indication that is 30 percent lower than the actual concentration. For these types of sample streams, water must be removed prior to NO_x detection, calibrating the detector with saturated span gas, or correcting the reading based on a third body quenching algorithm and measured water content.⁷

Similar calculations can be performed for other typical combustion exhaust products. Potential errors greater than 20 percent are not uncommon, even for fuel-lean conditions. Only for the extremely lean conditions associated with jet engines is dilution great enough to compensate for the third body effect. As a general rule, NO_x measurement error increases with increasing H/C ratio of the fuel and increasing equivalence ratio (Φ , defined as the actual fuel-air ratio divided by the stoichiometric fuel-air ratio). Measurements taken in very fuel-rich systems or in the fuel-rich regions of diffusion flames may be subject to even greater errors due to the potential presence of polyatomic fuel molecules with high quenching characteristics. The third body quenching effect is most important for sample streams that have large concentrations of non-diatomic constituents. If unaccounted for, third body quenching may be a significant source of error in NO measurement (generally low indication). In combustion exhaust with nitrogenous species other than NO, NO₂ and N₂, attention must be given to the conversion of these species to NO in the sampling system converter. Finally, cautious interpretation of NO_x

measurements from systems using catalytic converters should be made for any scenario where unburned hydrocarbons are present (e.g. fuel-rich combustion, diffusion flames).⁷

Chemiluminescent NO_x analyzers with associated sample conditioning equipment have been the systems of choice for measuring NO_x. The instruments are based on measuring the light emitted from an excited NO₂ molecule when it is formed between the reaction of ozone and nitric oxide (NO). While this technique can provide exceptional sensitivity (instruments developed for ambient measurements can have a lower detection limit of less than 0.1 ppb), these instruments measure only NO directly. Their response is also dependent on the concentration of water vapor, since water quenches the chemiluminescence from the reaction (a moisture removal system is typically employed upstream of the analyzer to remove water vapor). To measure NO₂, a reducing converter is added; this reduces the NO₂ to NO prior to detection. The “total NO_x” can then be detected as the original exhaust concentration of NO plus the NO concentration resulting from NO₂ to NO conversion. These converters are usually high-temperature devices (approximately 350°C) that contain a reducing surface, typically molybdenum or carbon, but stainless steel and gold surfaces have also been used successfully with reducing gases such as CO or H₂. While they are often called catalytic converters, in each case a reducing agent is expended over time.

With these applications, low concentration calibration gases are necessary. These calibration gases are much more difficult to produce and certify; therefore, they are more expensive. New certification standards and procedures may be needed for gas manufacturers in order to reduce costs.

A number of interim techniques have been developed in order to enable the measurement of very low NO_x concentrations. One such method is a CEMS spiking procedure where NO and NO₂ are injected at the sampling probe. In one study,⁴ NO₂ recovery was only 59 percent at 1.6 ppm, possibly because of the NO₂ solubility in sample conditioning system, low NO_x instrument bias, and low converter efficiency (85.4 percent). NO recovery was only 83 percent at 1.7 ppm. At 10 site studies, RATA tests varied from 1.3 percent to 34 percent [average was 9.16 percent, SD = 8.03 percent]. CO₂ causes interference with chemiluminescence, but was limited to 1 percent of the measured value for CO₂ concentrations up to 10 percent (gas turbine system exhaust is typically between 2 percent and 5 percent CO₂).⁴

Once the sample stream has been managed to prevent condensation, it is necessary to reduce the NO₂ to NO in the converter. This is a process that typically has at least 97 percent efficiency, but this efficiency can depend on the NO₂ concentration, the age and use history of the converter, and the matrix in which it is measured.

High temperatures in sampling system convert NO₂ to NO. The higher the temperature, the further the equilibrium is pushed toward NO. Heated stainless steel tubing is commonly used as an NO₂ to NO catalyst (T > 177 °C). Reaction occurs (at or above 177 °C), however, only when the surface of the stainless steel is oxidized. Brand-new stainless converts very little. Lower temperatures (T < 371 °C) favor the NO₂ side of equilibrium. Conversion from NO to NO₂, however, occurs at temperatures below 149 °C. The lower the temperature, the further the reaction is pushed toward NO₂. One study⁶ demonstrated NO₂ losses in condensate (across a condenser with water in the reservoir): At a total NO_x concentration of 690 ppm, initial NO₂ at 1 ppm led to a 4 percent NO_x loss, initial NO₂ at 232 ppm led to a 13 percent NO_x loss. Results

suggest NO to NO₂ conversion in cooled sample stream with subsequent NO₂ loss in condensate. Using a permeation dryer, all NO₂ was converted to NO within the dryer (using dry gas). The conclusion is that permeation dryers can give accurate total NO_x results, but not individual NO/NO₂ concentration measurements. Carbon converter efficiency is optimized at 349 °C < T < 399 °C. Ammonia can partially oxidize to NO in a stainless steel converter, leading to positive NO_x bias. In contrast, there is a negative NO_x bias through carbon converter when ammonia is present. NO and NH₃ have been known to disappear in parallel when passed over graphite at 510 °C. In the presence of SO₂ in flue gas, total NO_x remained the same, but NO ratio increased (believed to be caused by NO₂ reaction with SO₂ to form SO₃ and NO in the condenser). This issue can potentially be avoided by maintaining the condensate basic to keep NO₂ in solution (not able to react).⁶

Another problem with the chemiluminescent method is that the converters used to reduce NO₂ to NO can also oxidize ammonia (NH₃) to NO. The extent of ammonia conversion depends on many factors such as converter age, water content and matrix composition. With molybdenum-based converters, for example, the ammonia bias is typically a few percent of concentration, although the formation of molybdenum trioxide as the converter ages raises this conversion rate. NH₃, therefore, causes a positive interference. Evaluating this interference is particularly important when the sampled stream uses ammonia injection to reduce NO_x emissions.⁶

2.0 Approach

For conducting the laboratory testing, CE-CERT used a dilution calibration/gas blending system that enabled precise mixing of calibration gas standards and other effluent components to meet analyzer calibration requirements as well as the specified simulated stack gas concentrations. This high-volume unit allowed for simultaneous measurement using multiple NO_x measurement systems.

The CE-CERT dilution calibration/gas blending system, developed and constructed for other emissions research programs, was designed to meet the Code of Federal Regulations (CFR) specifications for calibration of vehicle and stationary source emission gas measurement systems as well as for the needs of a variety of research projects. The system included ten “new generation” mass flow controllers. The mass flow controllers, operated on digital signals, had a stated accuracy of 1 percent of set point. The systems allowed for the blending of multiple calibration gases (from ppb to percentage range concentrations) with one or more of several pure gases (e.g. nitrogen, zero air and carbon dioxide). For simulating stack gas moisture, deionized water was pumped through a flow-controlled piston pump and then through a heated column to obtain water vapor for humidifying the gas blend to the desired levels. Figure 1 shows a schematic of the dilution calibration/gas blending system.

The versatility of this system fit in ideally with the needs of the current project. This calibrator was used as a gas blender to mix calibration standards of nitric oxide (NO), nitrogen dioxide (NO₂) and ammonia (NH₃) with pure gases of nitrogen, zero air and carbon dioxide (CO₂) to obtain a broad spectrum of concentrations. The system was configured to provide dilute levels of NO₂ via dilution of NO₂ calibration gas. A more specific schematic of the dilution calibration/gas blending system is attached as Appendix I.

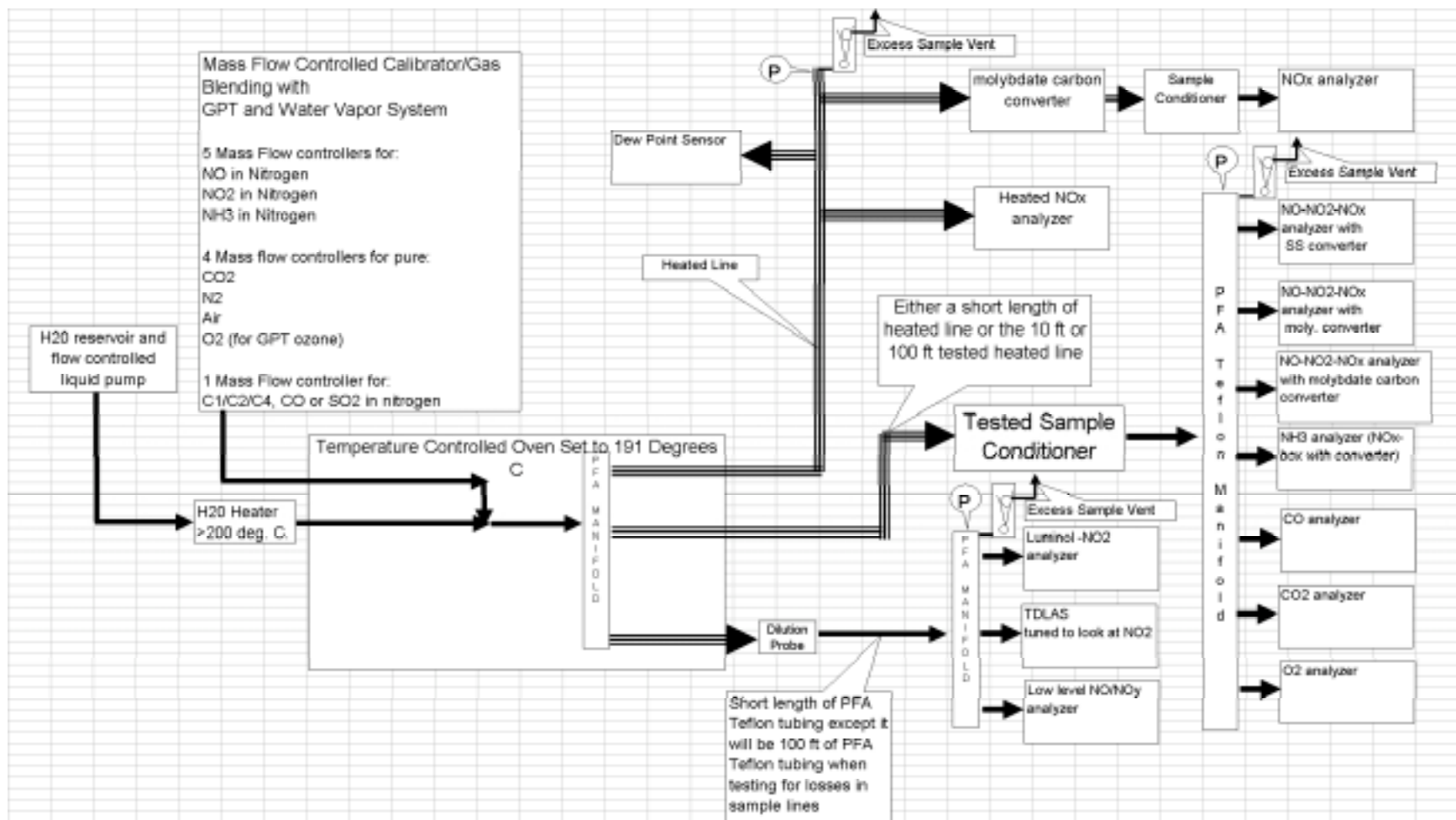


Figure 1: Dilution Calibration/Gas Blending System

2.1 Sampling and Analytical Equipment and Materials, and Procedures

2.1.1 NO_x Analyzers

For the dilution extractive analysis assuming a 50:1 dilution, a TECO Model 42CY chemiluminescence analyzer with a range of 1 ppb to 1.0 ppm was used. For all other analyses, TECO Models 42 and 10 chemiluminescence analyzers with full-scale ranges of 0-5 ppm and 0-100 ppm NO_x were utilized. Three dry chemiluminescence analyzers with different NO₂ to NO converters were evaluated simultaneously through all phases of the test program. Two other chemiluminescent analyzers were evaluated concurrently with the other instruments: one that was designed with a converter placed upstream of the sample conditioning system (CAI), and another designed to measure hot/wet sample streams. In addition, two other types of analyzers were employed to directly measure NO₂ from the manifold gas stream. The first instrument was based on tunable diode laser detection (TDL), manufactured by Unisearch, which was specifically tuned for NO₂. The second instrument, developed by CE-CERT, was an NO₂/PAN gas analyzer based on the principle of chromatographic separation with luminol detection. The luminol chemiluminescent approach is attractive for measurements of low concentrations of NO₂ because of its high sensitivity and rapid response, its simplicity, and selectivity to NO₂ relative to other nitrogenous species. With traditional chemiluminescence, heated NO₂ to NO converters are employed, as the instrument measures only the reaction of NO with ozone. In the heated converters, several other nitrogen species (HNO₃, HNO₂, organic nitrates, peroxyacetyl nitrate [PAN]) are converted to NO, making it impossible to specifically quantify NO₂ by difference between NO_x and NO readings. The luminol technique, however, is subject to interference, and exhibits non-linear response at NO₂ concentrations less than a few ppbv. As a result, careful operation and corrections for interferences and non-linearity are required in order to obtain accurate measurements at low NO₂ concentrations. Ozone is an interferent, but only at very low (<10 ppbv NO₂) concentrations.⁸ These instruments were used as a quality control measure, enabling direct NO₂ measurement independent of potential ambiguities resulting from using NO₂ converters.

Analyzer calibration was accomplished with EPA Protocol gases blended with pure diluents in the dilution calibration/gas blending system. An independently prepared NO calibration gas standard, traceable to the NIST standards, was used to confirm the stability of calibration gases. The analyzers' converters were checked utilizing NO₂ gas standards. Table 1 lists the operating parameters for each of the NO_x analyzers used during the program.

Table 1: Chemiluminescence NO_x Analyzer Parameters

Factory Specs	Model 42 and 42C (ambient)		
	Operating range	Sample	Ozone
NOx-1 (TE-42 "Hello")-molybdate converter followed by sample conditioner	amb:100 ppm, source 5000 ppm	15 mm, 700 cc/min	8 mm, 100 cc/min
NOx-2 (TE-42 "AV#1") - standard internal TE SS converter	10 ppm	200 cc/min	no change made
NOx-3 (TE-42C loaned from TE) - standard internal TE molybdenum converter	10 ppm	30 cc/min	no change made
NOx-4 (TE-42 "AV#2) - external molybdate carbon converter	10 ppm	126 cc/min	no change made
NOx-5 (TE-42C loaned from TE) - external NH3 converter	10 ppm	22 cc/min	no change made
NOx-6 (TE-42CY APL's) - dilution probe -> std internal TE molybdenum converter	20 ppm	no change made	no change made
	200 ppb	no change made	no change made
		Model 42H and 42HL (source)	
NOx-7, NOx-8 (TE-42) - standard internal TE SS converter		5 mm, flow not specified	10 mm, 200 cc/min

2.1.2 Other Gaseous Analyzers

For determination of simulated stack gas compositions, the following instruments were used:

- NH₃: TECO Model 42 with high temperature (800 °C) converter
- CO₂: Horiba Models AIA-23 and OPE-135 non-dispersive infrared detection with flow modulation
- O₂: Horiba Model CMA-331A paramagnetic pressure detection
- CO: Horiba Models CFA-26 and OPE-144 non-dispersive infrared detection with optical filter
- Dew Point (stack gas): General Eastern HYGRO-M1 chilled mirror with heated case sensor
- Dew Point (ambient): General Eastern 1200 MPS chilled mirror with platinum RTD temperature

2.1.3 Sample Conditioning Systems

The following sample conditioning systems were evaluated:

- A dilution extractive system
- A permeation dryer with ammonia removal
- A thermoelectric (impinger-type) cooler
- A refrigerated (coil-type) condenser
- An EPA Method 5-style impinger train in an ice bath
- A dual technique system (ambient temperature water removal followed by permeation dryer)

2.1.4 Sample Lines

The following heated sample line materials were evaluated:

- PFA Teflon
- 316L stainless steel
- 316L Silcosteel® (stainless steel with a thin glass lining)

The three sample lines (approximately 100 ft. long) were bundled into a single heated wrapping and equipped with temperature controllers to allow for testing at multiple temperatures.

2.1.5 Simulated Stack Gas

To simulate typical low-NO_x effluents, it was necessary to generate wet and dry gas streams at flow rates of approximately 12 liters/minute. The streams contained constant blends of N₂, O₂, and CO₂. These blends were generated from pure CO₂ and N₂ (available in-house at CE-CERT) and zero air cylinders using the dilution calibration/gas blending system described in Section 2.0. Precise mass flow-controlled quantities of NO and NO₂ from calibration gas cylinders were injected into the simulated stack gas stream to produce the concentrations investigated in this

study. To generate the wet gas streams, controlled injection of deionized water into a heated (191°C) simulated stack gas stream was performed.

2.1.6 Additional Evaluation of Ammonia Effects

The initial NO_x measurement evaluations with added ammonia gave unexpected and seemingly inconsistent results. Additional testing was performed to more conclusively determine potential problems in measuring NO_x and NH₃. To evaluate the penetration of ammonia through sample conditioners and lines, synthetically prepared mixtures were again analyzed by chemiluminescent analyzers with and without these components installed. The following describes the experimental setup, the matrix of experiments performed, and the results obtained.

Synthetic Exhaust

The system to generate the synthetic exhaust was similar to that originally used but simplified to focus on the ammonia addition evaluation. Figure 2 shows the system used to generate the synthetic exhaust. Mass flow controllers were used to blend the synthetic exhaust mixture. A PC was used to control these devices and to continuously record their status and mass flow rate. The gases blended from compressed gas sources were:

- Ammonia
- Nitrogen
- Oxygen
- CO₂
- NO
- NO₂

In addition, water vapor was added when needed by means of a liquid pump operated at 191°C as described previously. Concentrations were calculated from the flow rates of the various components added.

Measurements

To measure the combined concentration of NO_x and NH₃, a high-temperature (800 °C) stainless steel converter was used to convert NO₂ and NH₃ to NO. The concentration of NO was then quantified with a ThermoEnvironmental Instruments (TEI) model 42 chemiluminescent analyzer. The analyzer was plumbed into a common manifold where all NO_x analyzers were located. Three chemiluminescent analyzers were used to measure the concentrations of NO_x. All were TEI source level (or converted to source level) chemiluminescent instruments with different converters:

- Stainless steel (350°C)
- Pure molybdenum (350°C)
- Molybdate carbon (350°C)

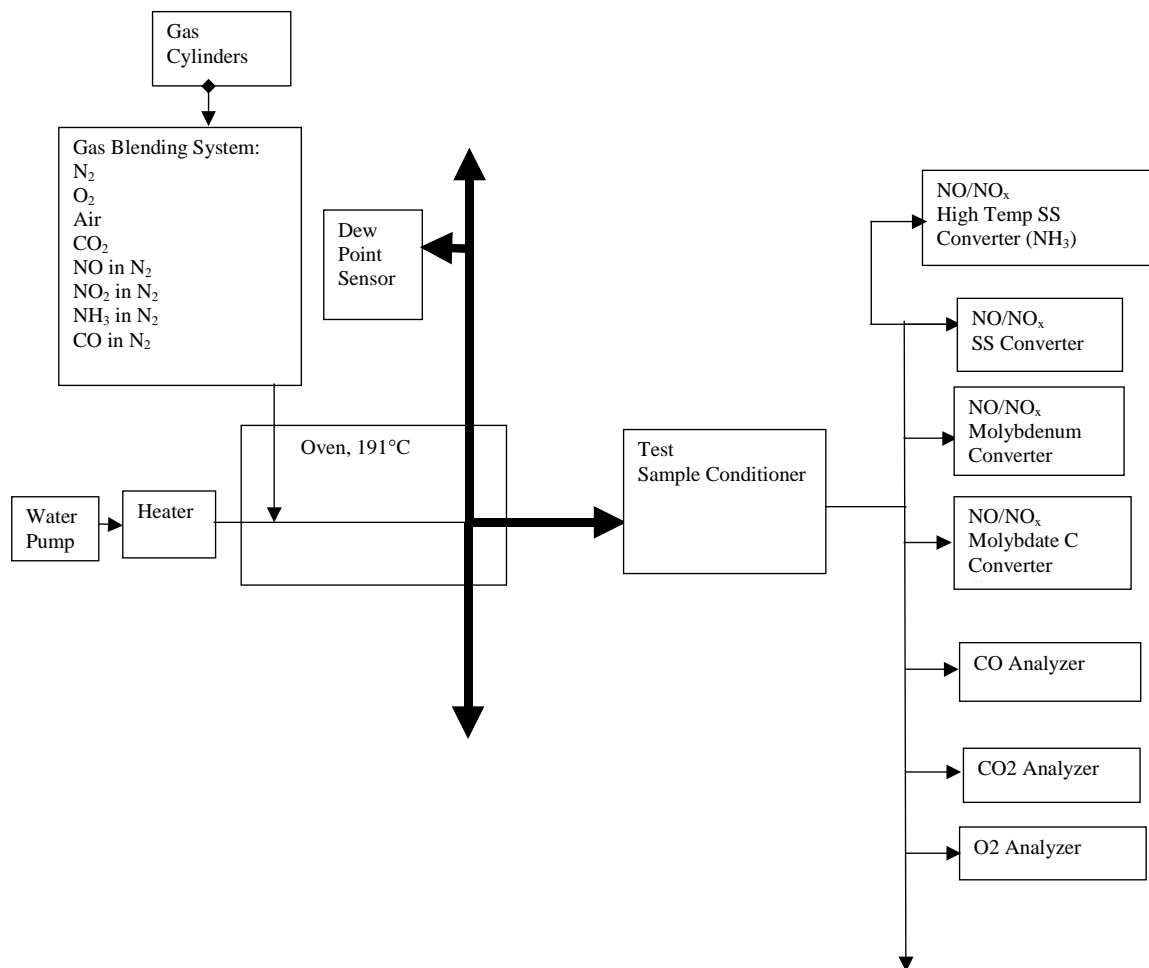


Figure 2: Schematic of Test System used to Determine Ammonia Penetration

To measure NH_3 in the presence of NO_x , it was necessary to subtract the average NO_x measured from the two instruments that demonstrated no NH_3 conversion (analyzers with molybdenum and molybdate carbon) from the $\text{NO}_x + \text{NH}_3$ obtained from the high temperature converter analysis system).

NH_3 and Water Combinations Only in N_2/O_2

The tests were first conducted using only ammonia (nominal calculated concentration of 15 ppmd) in an ambient O_2/N_2 mixture with and without added water (nominally calculated as 6 or 13 percent @ 191°C). These test gases, as well as all others, were prepared in an oven at 191°C. Each test point consisted of 20 minutes of sampling, with the results calculated from the average of the second-to-last minute of sampling. The objectives of these tests were to determine the penetration of ammonia through the sampling systems before adding NO_x to the system and to determine the NH_3 interference of each NO_x analyzer/converter combination. One of three methods of water removal was used prior to introduction to a NO_x analyzer: refrigerated condenser, thermoelectric chiller, and glass impingers in an ice bath. For these

tests, the sample line between the oven and sampling manifold was a minimum length of heated (140°C) PFA Teflon.

Using the thermoelectric chiller as the reference sample conditioner, another set of tests were conducted with 100 feet lengths of Silcosteel[®], stainless steel, and PFA Teflon to evaluate ammonia losses at three different line temperatures. Table 2 summarizes the mixtures tested.

Table 2: Summary of Tests Conducted in N₂ and O₂ with added NH₃ and H₂O

Test#	Refrig	Ice Bath	Chiller	Min Line	PFA Line	Silco Steel Line	SS Line
1a	X			X			
2a		X		X			
3a			X	X			
4a			X		X		
5a			X			X	X
6a			X				X

NH₃ and NO_x in Simulated Exhaust

In the second series of tests, the matrix air was changed to simulate exhaust by reducing the oxygen content to 15 percent and adding four percent CO₂. To this mixture NH₃ was added (nominally 7 or 12 ppmd) and two concentrations of water were added (6 or 13 percent @ 191°C). Tests were conducted without added NO_x and for two concentrations of NO_x (nominally 0.44 and 9.7 ppmd) with equal concentrations of NO and NO₂. Both the refrigerated condenser and thermoelectric chiller sample conditioning systems were evaluated. Otherwise, the experimental set up was exactly the same as that for the tests with ammonia alone. Table 3 summarizes the experimental plan. The objectives of this portion of the study were to determine what effect the addition of CO₂ and reduction of oxygen would have on the response of NO_x analyzers with various types of converters and the effect of adding NO_x to the simulated exhaust gas.

Table 3: Summary of tests Conducted in Simulated Exhaust with Added NH₃ and NO_x

Test#	Refrig	Chiller	Min Line	Stainless Steel Line	PFA Line	13% H ₂ O	6% H ₂ O	7ppm NH ₃	12ppm NH ₃
1b	X		X			X		X	
2b	X		X			X			X
3b	X		X				X		X/0
4b		X	X			X		X	
5b		X	X			X			X
6b		X	X				X		X/0
7b		X		X		X		X	
8b		X		X		X			X
9b		X		X			X		X/0
10b		X			X	X		X	
11b		X			X	X			X
12b		X			X		X		X/0

3.0 Preliminary Assessment of Potential Problems

Before experimental work was undertaken, we conducted a review to identify potential problems with existing regulatory methods for gaseous pollutant measurements at concentrations expected to be typical for new power plants. The objective of this task was to assess potential interferences and uncertainties when measuring carbon monoxide (CO), volatile organic compounds (VOC), and air toxics in the exhausts from power plants, especially those designed for low-NO_x emission characteristics.

3.1 Approach

The approach was to perform a search to determine what has been reported with respect to the measurements given in the objective. The primary approach was a literature search to determine what had been published. This was done using the California Digital Library (CDL) to search the UC library (Melvyl) and Current Contents databases. The former contains all types of books, periodicals, and reports while the latter focuses on journal articles published within the past 15 years. Keywords for exhaust, such as exhaust and emissions, were combined with others such as CO, carbon monoxide, volatile organic carbon, VOC, and air toxics. Since the latter three are general topics, we also focused on more specific keywords such as non-methane hydrocarbons, NMHC, aldehydes, formaldehyde, and butadiene. Titles found by the databases were reviewed and either abstracts or full papers of applicable titles were obtained. These references were reviewed and applicable references cited were added to the literature compiled. Applicable references involved measurement of the target pollutants or classes in exhaust gases. This approach was the primary technique to find references that were published prior to the start of the electronic data base compilation. A synopsis of all the relevant literature is presented.

A second source of information was obtained from interviewing people who are involved with this research area for references and personal relevant information.

3.2 CDL Literature Search

Table 4 and Table 5 show the keywords, database, number of references listed, and the number of applicable references for the Current Contents and the Melvyl databases, respectively. The applicable references are listed.

Table 4: CDL Literature Search of the Current Contents Database

Key Words	# Refs	# App Refs	Ref ID	Comments
Exhaust	1469	?		Too large of category
Exhaust+VOC	1	0	1	Mobile source
Exhaust+ Toxic	2	0		Mobile source
Exhaust+Turbine	26	6	2-7	Mostly aircraft turbines
Exhaust + CO	12	0		
Exhaust+Carbon Monoxide	16	2	8-9	Mobile sources
Exhaust+Aldehyde	0	0		
Exhaust+Formaldehyde	3	1	10	Mobile source
Exhaust+Acetaldehyde	1	1		Same as above
Exhaust+Butadiene	2	0		Mobile sources
Exhaust+Hazardous	0	0		
Exhaust+NMHC	0	0		
Exhaust+Non-Methane Hydrocarbon	1	0		Mobile source
Emissions	6453	?		Too large of a category
Emissions+Turbine	21	1	11	
Emission+Turbine	15	1	12	
Emission+dioxin	16	1	20	
Emissions+VOC	94	0		Key word not appropriate
Emissions+Power Plant	25	1	13	Coal-fired
Turbine	2687	?		Too large of a category
Turbine+VOC	0	0		
Turbine+Toxic	0	0		
Turbine+CO	3	0		Co-Generation
Turbine+Carbon Monoxide	1	1	11	Repeat
Turbine+Aldehyde	0	0		
Turbine+Formaldehyde	0	0		
Turbine+Acetaldehyde	0	0		
Turbine+Butadiene	0	0		
Turbine+Hazardous	0	0		
Turbine+NMHC	0	0		
Turbine+Non-Methane Hydrocarbon	0	0		

Table 5: CDL Literature Search of Melvyl Catalog

Key Words	# Refs	# App Refs	Ref ID	Comments
Exhaust	643	?		Too large of category
Exhaust+VOC	0	0		
Exhaust+ Toxic	10	2	14,15	Mobile sources
Exhaust+Turbine	15	0		Standard testing
Exhaust + CO	3	0		
Exhaust+Carbon Monoxide	3	0		
Exhaust+Aldehyde	0	0		
Exhaust+Formaldehyde	4	0		
Exhaust+Acetaldehyde	0	0		
Exhaust+Butadiene	0	0		
Exhaust+Hazardous	0	0		
Exhaust+NMHC	0	0		
Exhaust+Non-Methane Hydrocarbon	0	0		
Emissions	>1000	?		Too large of category
Emissions+Turbine	19	2	16,17	
Emission+Turbine	10	2	18,19	
Emissions+VOC	33	0		None exhaust related
Emissions+Power Plant	24	0		
Turbine	>1000	?		Too large of category
Turbine+VOC	0	0		
Turbine+Toxic	0	0		
Turbine+CO	9	0		"CO" found as company
Turbine+Carbon Monoxide	0	0		
Turbine+Aldehyde	0	0		
Turbine+Formaldehyde	0	0		
Turbine+Acetaldehyde	0	0		
Turbine+Butadiene	0	0		
Turbine+Hazardous	0	0		
Turbine+NMHC	0	0		
Turbine+Non-Methane Hydrocarbon	0	0		

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- E. Feitelberg, A.S.; Chalfin, J.; Totosian, J.; Schorr, M.M.; Summer, J.W.; and Sabla, P.E. (1997) Survey of gas turbine hazardous air pollutant emission factors. Air and Waste Management Association 90th Annual Meeting. June 8-13, Toronto, Canada.

From a review of the titles it is clear that none of the references obtained clearly focuses on the objectives of better understanding the artifacts and uncertainties when sampling burner or power plant exhaust for carbonaceous air pollutants. One reason for this lack of reported research may be that many pollutants, in general, are at concentrations that are difficult to measure in the exhaust from external combustion sources. Given rapid dilution after release, it is unlikely that these sources could result in a measurable increase in the atmospheric burden of

these pollutants. Table 6 summarizes the concentrations of various pollutants measured in a number of different combustion sources. In many cases the concentrations are so close to typical ambient concentrations that it is not clear whether the combustion is a pollutant generator or destroyer. As an example, Hilton et al. (1998) could quantify CO only at idle, at full continuous load the CO concentrations dropped below 20 ppm, not much more than typical ambient concentrations. For aircraft turbines, the most comprehensive measurement of trace organic pollutants was reported by Spicer and co-workers in 1994. C₁-C₁₇ gases were quantified by gas chromatography while particulate samples were extracted and analyzed by gas chromatography with mass spectrometric detection. While informative, these results obviously do not apply to the new generation of turbines used for power plants.

Table 6: Summary of Pollutant Concentrations measured in External Combustion Sources

Pollutant	Range, ppm	SourceType	Ref#	Comments
CO	50-250	Turbine	2	Idle
CO	2-42	Turbine	11	Full load
HAP	0.005-1	Burner	D	Individual species, normal load
HAP	0-0.05	Turbine	E	All species, normal load

Measurements at concentrations near the normal analytical detection limits are difficult to make, and there were no reports on the potential artifacts that may occur under low concentration conditions in a hot mix of co-pollutants. Comprehensive studies are therefore needed using *in situ* spectroscopic methods that would minimize measurement artifacts. Non-extractive methods would also allow direct measurement without the need for water management that may result in sampling artifacts, unproductive dilution, or both. Infrared spectroscopy, either using Fourier Transform or tunable diode laser technology would be a recommended approach for compound with significance absorbance (CO, for example) and may be useful for other compounds with multiple pass absorption cells (NO₂, for example). Hilton et al. (1998), for example, showed large differences in CO concentration between extractive and non-extractive techniques for gas turbines at idle. For organic compounds, direct sampling and measurement using dual mass spectrometric methods for sample identification followed by quantification offers an analytical method that is unlikely to involve sampling artifacts. Less polar organic compounds could also be selectively trapped to increase the analytical sensitivity and to remove water vapor prior to gas chromatographic analysis.

Since many pollutant concentrations are generally at very low concentration in turbine exhaust, it may be useful to focus on the most toxic compounds that are likely to found in the exhaust. Dioxins and furans are classes of chemical that can cause adverse health effects at extremely low concentrations. These compounds have been shown to form in the exhaust of diesel engines in which there was no significant source of chlorine in the fuel (Gertler et al., 1998). Presumably, the source of chlorine was salt containing particulate matter in ambient air. This salt would be found primarily near coastal areas. The potential for these emissions from power plants near the coast should be evaluated with measurements.

4.0 Outcomes

All testing was conducted indoors with the ambient temperature of the test room maintained between 18°C and 29°C at all times during the test. The ambient air temperature during these tests was controlled to within $\pm 4^\circ\text{C}$ from the ambient air temperature determined as the average of the air temperatures measured before and after each test. The relative humidity was maintained between 20 percent and 65 percent during all tests. It was monitored throughout each set of tests.

4.1 Analytical Instrument Performance Testing

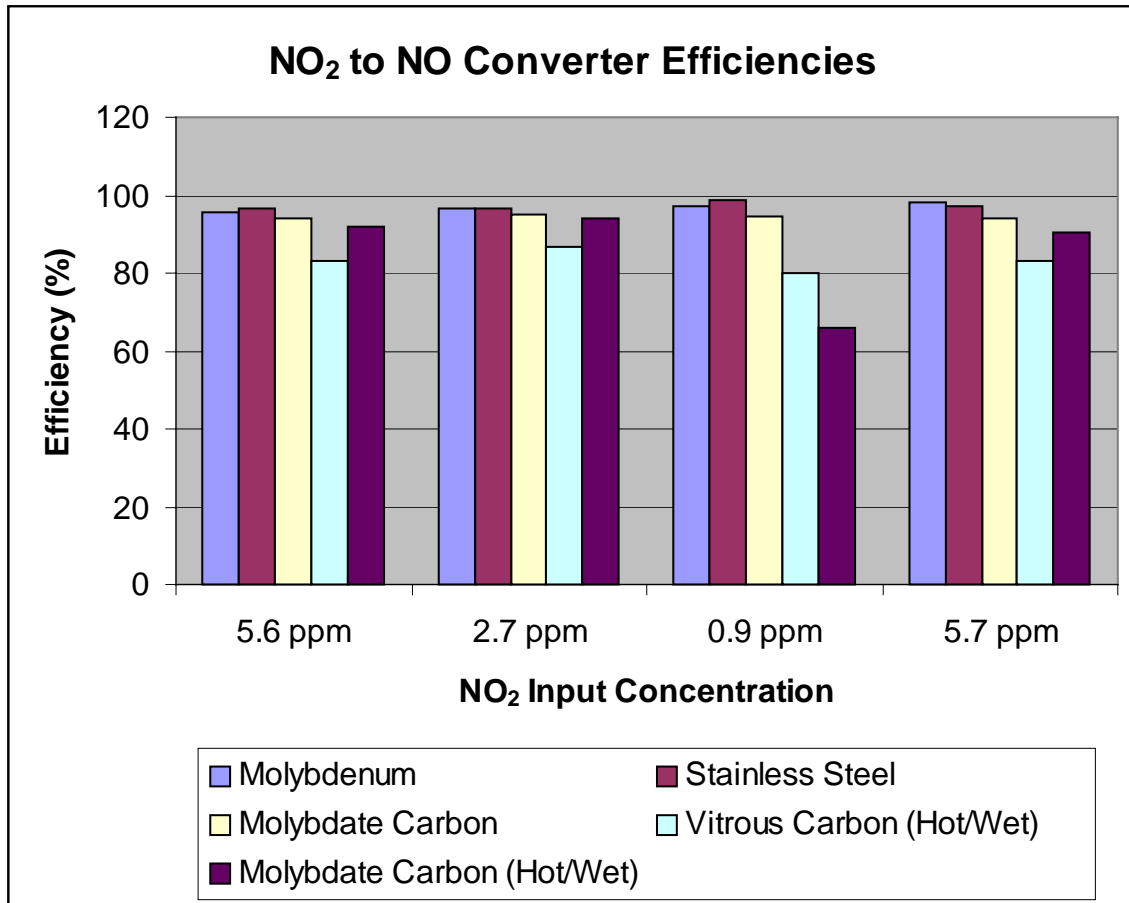
Before evaluation of sample conditioning systems, each of the specified analyzers was run through performance testing for determination of linearity, cross-sensitivity, and calibration/zero drift. Each of the analyzers was “zeroed” by injecting CEM-grade N_2 directly into the analyzer. Each analyzer was then be “spanned” by injecting USEPA Protocol NO at 80 percent and 40 percent of each applicable range. A Quality Assurance/Quality Control (QA/QC) audit was performed for the instrument performance tests. A summary of the QA/QC audit report is included in Appendix III.

4.1.1 NO_2 to NO Converter Efficiencies

Each of the analyzer converters was evaluated for conversion efficiencies by injecting certified NO_2 concentrations at 60 percent, 30 percent, and 10 percent of span for each applicable range. Figure 3 presents average conversion efficiency results from chemiluminescent analyzers using five different types of NO_2 to NO converters.

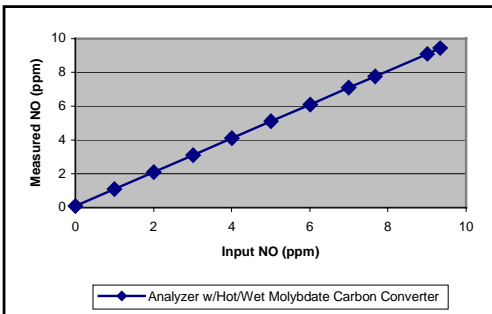
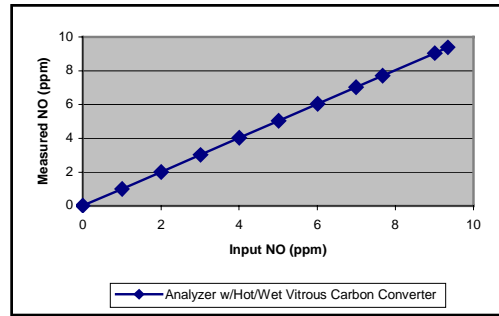
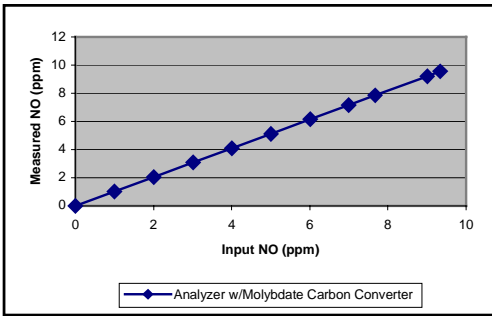
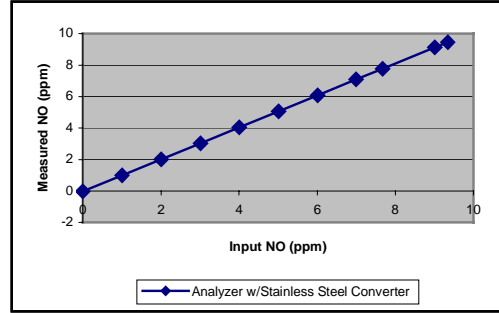
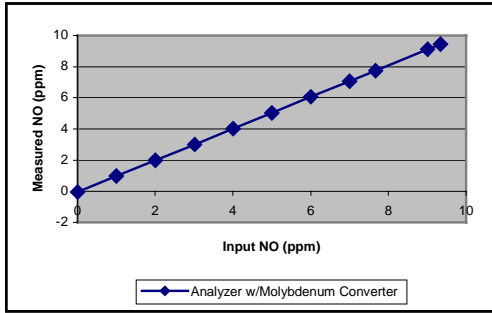
4.1.2 Calibration Curve (Linearity)

A gas divider and certified gas standards were used in order to establish the calibration curve for each NO_x analyzer. Full-scale span gas was introduced into the converter inlet of each analyzer to verify the calibration. The span value was recorded, and the concentration of the span gas was varied 100 to 0 percent in 10 percent increments using the dilution calibrator. Each analyzer was allowed to stabilize for at least two minutes at each point to account for the response time. This procedure was repeated to provide triplicate readings at each incremental point. Figure 4 presents results of the linearity testing of each analyzer.



Converter Type	Average NO ₂ /NO Converter Efficiency (%)
Molybdenum	96.9%
Stainless Steel	97.3%
Molybdate Carbon	94.3%
Vitrous Carbon (hot/wet)	83.3%
Molybdate Carbon (hot/wet)	85.5%

Figure 3: Average Conversion Efficiency Results from Chemiluminescent Analyzers using Five Different Types of NO₂ to NO Converters



Analyzer by Converter Type	Slope m	Intercept b	Correlation
Molybdenum	1.0153	-0.041	0.9999
Stainless Steel	1.0154	-0.0208	1.0000
Molybdate Carbon	1.0223	0.0037	0.9999
Vitrous Carbon (hot/wet)	1.0036	0.0101	0.9997
Molybdate Carbon (hot/wet)	1.0010	0.0904	0.9985

Actual Value = (m) x (Measured Value) + b

Figure 4: Analyzer Linearity

4.1.3 Cross-Sensitivity Test

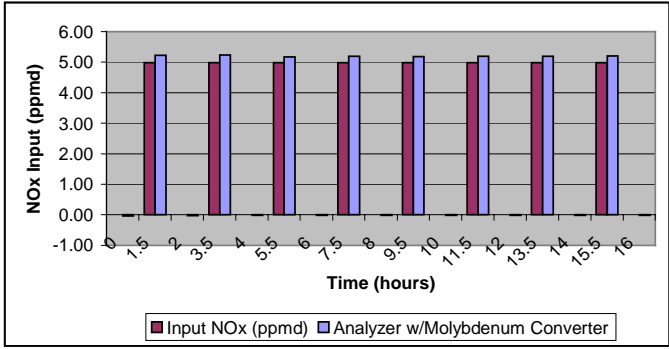
Each NO_x analyzer was zeroed with CEM-grade nitrogen. Each potential interferent gas was introduced consecutively into the analyzers along with various NO/NO₂ concentrations. The instruments' response to each of the interference gases was measured and recorded. Table 7 presents the average positive or negative bias recorded by each analyzer resulting from each interferent gas.

Table 7: Interferent Biases

Analyzer by Converter Type	NOx Analyzer Response (ppm, dry)			
	NH ₃ 6 ppm	NH ₃ 10 ppm	HC Mix 1000 ppm	CO ₂ 4%
Molybdenum	0.2	0.4	0.0	0.0
Stainless Steel	2.0	7.0	-0.3	0.0
Molybdate Carbon	1.0	1.5	0.0	N/A
Vitrous Carbon (hot/wet)	0.0	0.0	0.0	0.0
Molybdate Carbon (hot/wet)	0.1	0.1	0.0	0.0

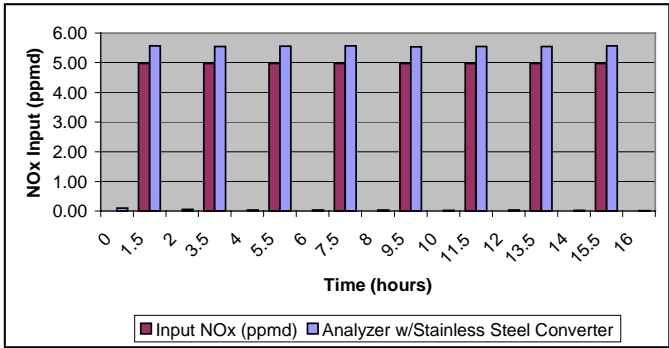
4.1.4 Calibration/Zero Drift Test

Each analyzer was calibrated at the beginning of the test. A calibration check (zero/span gas) was performed after sampling periods of at least two, four, and six hours. The analyzers would not be recalibrated or modified during the course of the drift tests. Calibration/zero drifts were calculated for each analyzer for each of at least two-hour time increments during the course of the test. Figure 5 presents results of the drift tests.



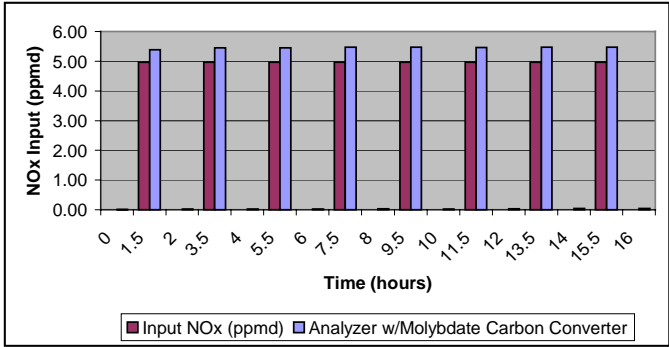
NO _x input	0	4.97
Time (hours)	Zero Resp.	NO _x Resp.
0	-0.05	5.22
2	-0.03	5.22
4	-0.02	5.17
6	-0.02	5.19
8	-0.02	5.18
10	-0.02	5.19
12	-0.02	5.19
14	-0.02	5.20

Time (hours)	6	10	14
Zero Drift	0.25%	0.22%	0.26%
NO _x Drift	-0.34%	-0.29%	-0.24%



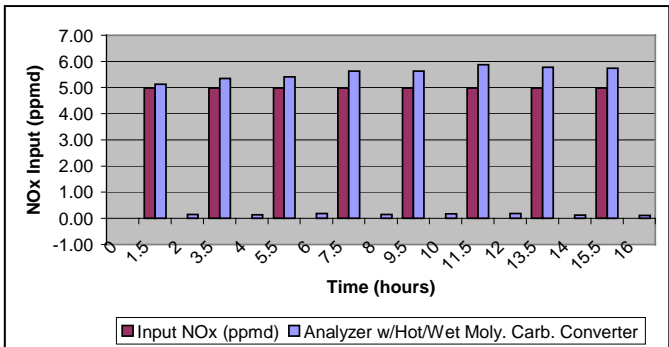
NO _x input	0	4.97
Time (hours)	Zero Resp.	NO _x Resp.
0	0.10	5.56
2	0.05	5.55
4	0.04	5.56
6	0.03	5.58
8	0.03	5.54
10	0.02	5.55
12	0.03	5.55
14	0.02	5.58

Time (hours)	6	10	14
Zero Drift	-0.65%	-0.72%	-0.74%
NO _x Drift	0.14%	-0.08%	0.13%



NO _x input	0	4.97
Time (hours)	Zero Resp.	NO _x Resp.
0	0.00	5.39
2	0.02	5.46
4	0.02	5.46
6	0.03	5.48
8	0.03	5.47
10	0.02	5.47
12	0.03	5.47
14	0.03	5.48

Time (hours)	6	10	14
Zero Drift	0.21%	0.20%	0.29%
NO _x Drift	0.82%	0.72%	0.82%



NO _x input	0	4.97
Time (hours)	Zero Resp.	NO _x Resp.
0	0.00	5.13
2	0.15	5.36
4	0.14	5.40
6	0.19	5.62
8	0.15	5.63
10	0.17	5.88
12	0.18	5.78
14	0.12	5.73

Time (hours)	6	10	14
Zero Drift	1.92%	1.71%	1.24%
NO _x Drift	4.92%	7.48%	6.07%

Figure 5: NO_x Analyzer Calibration/Zero Span Drift Test

4.2 Measurement System Performance Testing

CE-CERT conducted an extensive series of tests to evaluate performance of conditioning systems, heated lines, and effects of ammonia. Appendix II presents the detailed test matrix.

4.2.1 Evaluation of Sample Conditioning Systems

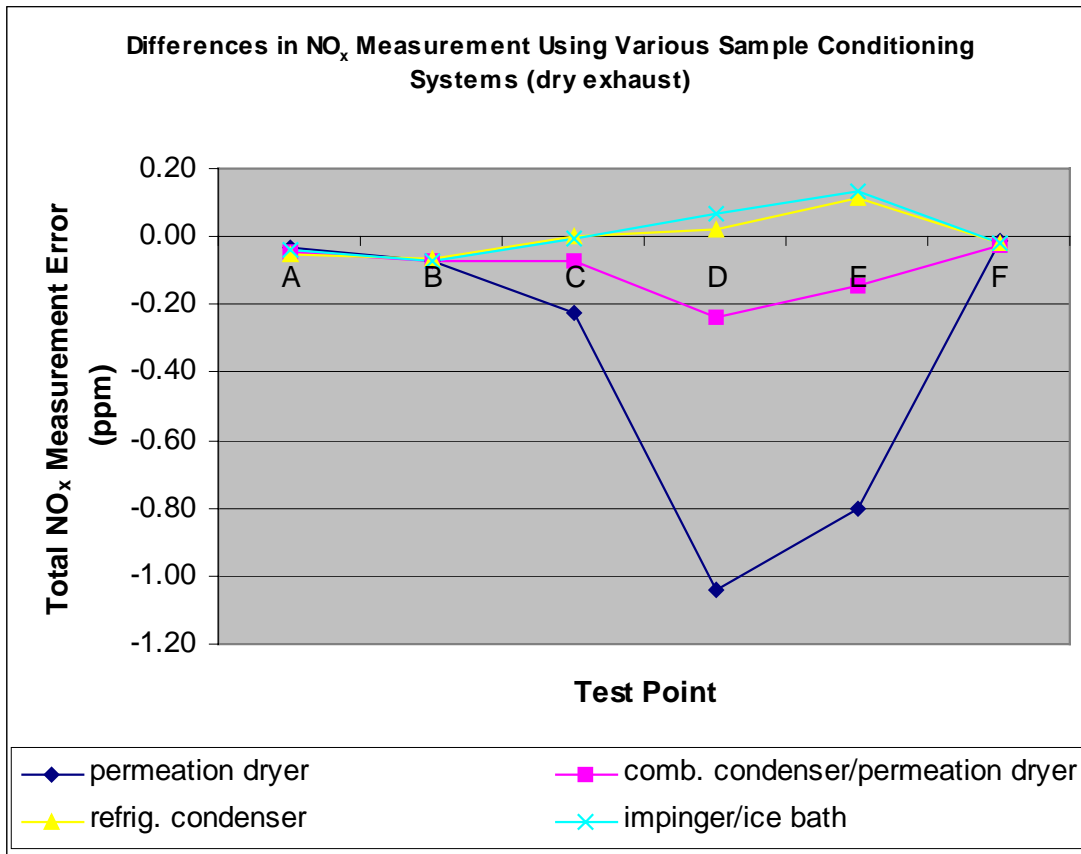
CE-CERT evaluated each of six types of sample conditioning systems:

1. A dilution extractive probe
2. A permeation dryer with ammonia removal
3. A thermoelectric (impinger-type) cooler
4. A refrigerated (coil-type) condenser
5. A glass impinger train submersed in an ice bath
6. A typical dual technique system (ambient temperature water removal followed by permeation dryer)

In each case, the outlet of the conditioning system was connected to the analyzer manifold with PFA Teflon tubing. Before testing, the analyzers were calibrated according to the procedures detailed in Section 2.1.1. The NO_x analyzer with the molybdenum converter was chosen as the reference analyzer for evaluating the sample conditioning systems, due to its low response to ammonia and high NO₂/NO converter efficiency. During all testing, the NO_x analyzer acquired sample from the analyzer manifold. The dilution extractive probe was evaluated along with the sample line testing. The other five types of sample conditioning systems were evaluated sequentially using various combinations of the nominal sample stream matrix in Table 8. Total NO_x Measurement Error in all of the figures is defined as the difference between measured concentrations and input concentrations (from mass flow controller set points). All NO_x measurements and results (Figure 6, Figure 7, Figure 8, Figure 9, Figure 10, and Figure 11) are presented on a dry basis.

Table 8: Simulated Exhaust Sample Test Matrix

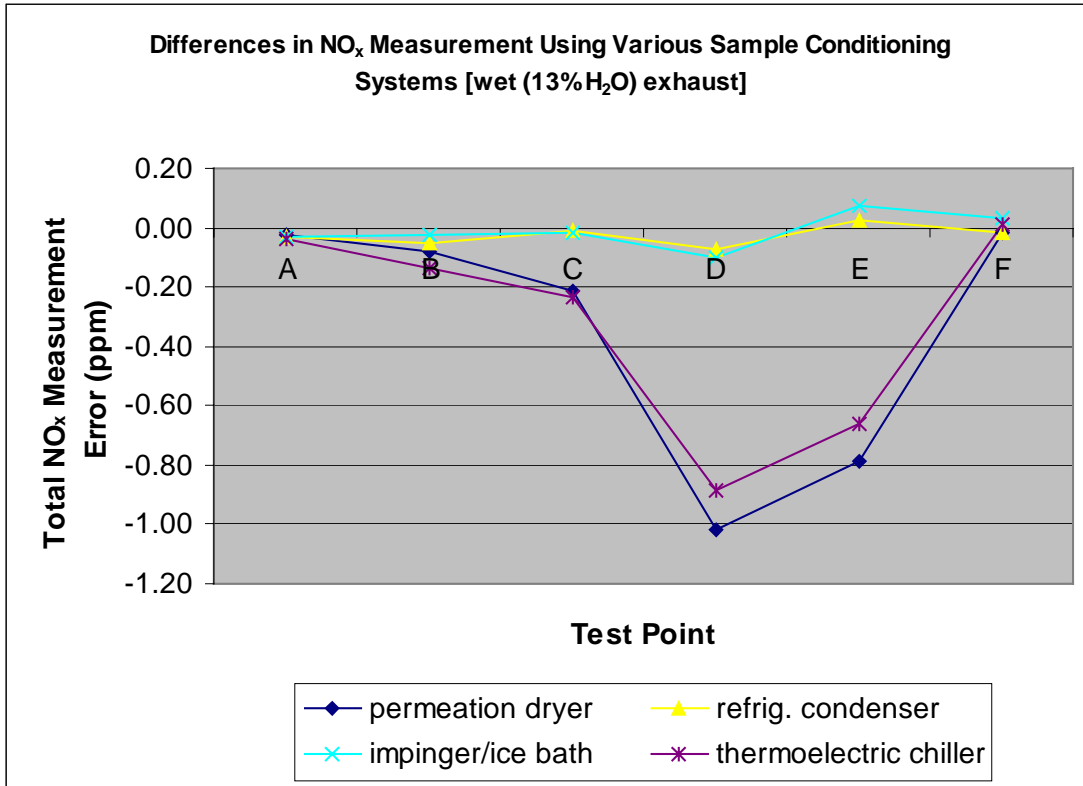
Dry Stack Gas (75% N ₂ , 10% O ₂ , 15% CO ₂)				Wet Stack Gas (dry stack gas + DI water)			
NO conc. (ppm, dry)		NO ₂ conc. (ppm, dry)		NO conc. (ppm, dry)		NO ₂ conc. (ppm, dry)	
0.2	1	5	9	0.2	1	5	9



Simulated Exhaust Conditions	
Component	Concentration (dry basis)
CO ₂	4%
O ₂	15%
NH ₃	0 ppm
Moisture	
	0%

Test Point	Nominal NO (ppm)	Nominal NO ₂ (ppm)	Nominal NO _x (ppm)
A	0.00	0.00	0.00
B	0.20	0.20	0.40
C	1.00	1.00	2.00
D	5.00	5.00	10.00
E	9.00	1.00	10.00
F	0.00	0.00	0.00

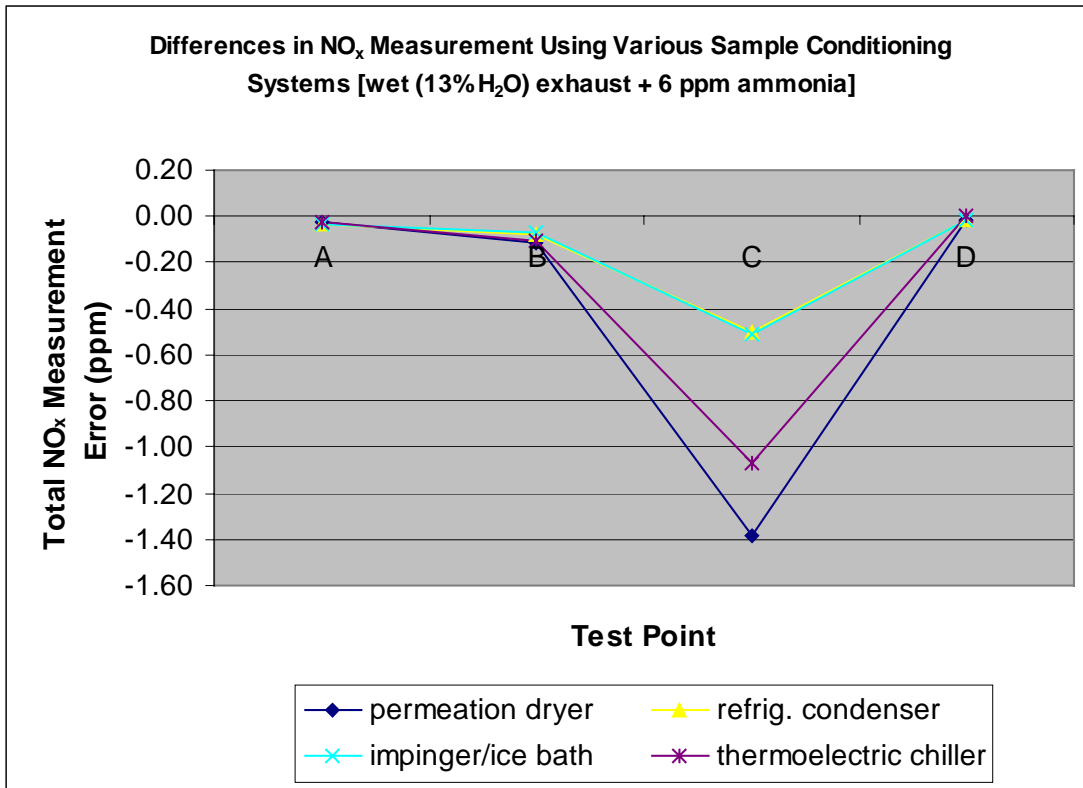
Figure 6: NO_x Measurement Differences with Simulated Dry Turbine Exhaust through Sample Conditioning Systems



Simulated Exhaust Conditions	
Component	Concentration (dry basis)
CO ₂	4%
O ₂	15%
NH ₃	0 ppm
Moisture	13%

Test Point	Nominal NO (ppm)	Nominal NO ₂ (ppm)	Nominal NO _x (ppm)
A	0.00	0.00	0.00
B	0.20	0.20	0.40
C	1.00	1.00	2.00
D	5.00	5.00	10.00
E	9.00	1.00	10.00
F	0.00	0.00	0.00

Figure 7: NO_x Measurement Differences with Simulated Wet (13%) Turbine Exhaust through Sample Conditioning Systems

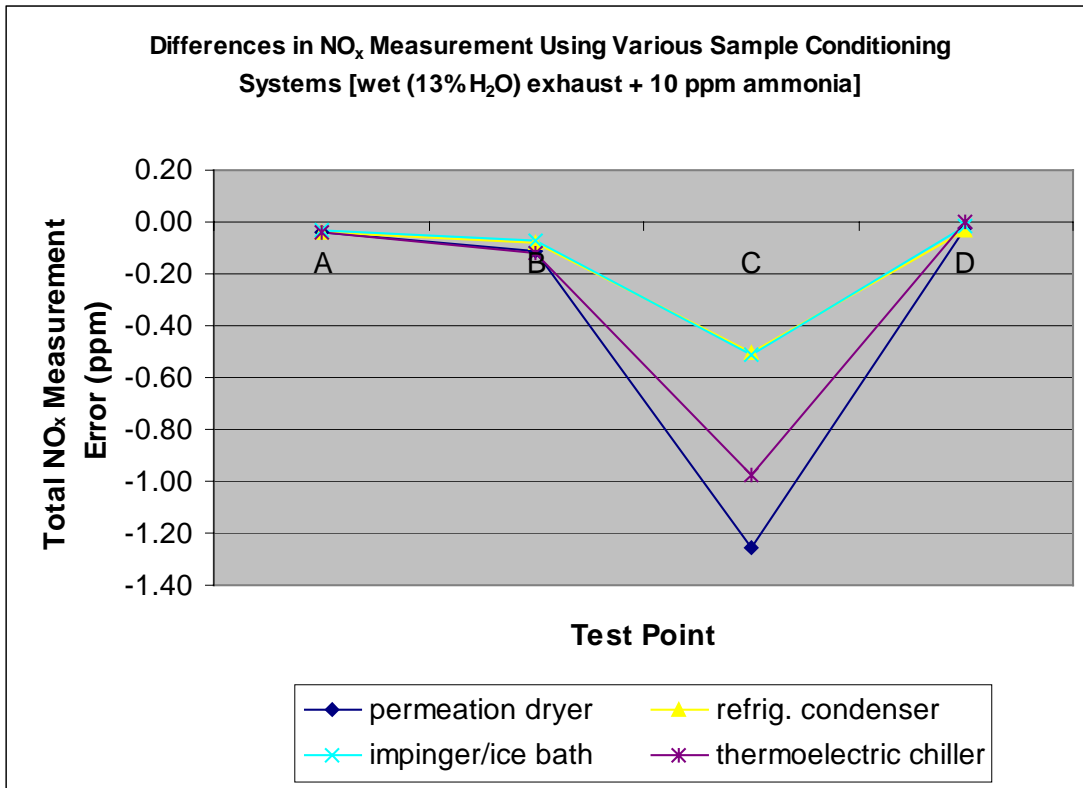


Simulated Exhaust Conditions	
Component	Concentration (dry basis)
CO ₂	4%
O ₂	15%
NH ₃	6 ppm

Moisture	13%
----------	-----

Test Point	Nominal NO (ppm)	Nominal NO ₂ (ppm)	Nominal NO _x (ppm)
A	0.00	0.00	0.00
B	0.20	0.20	0.40
C	5.00	5.00	10.00
D	0.00	0.00	0.00

Figure 8: NO_x Measurement Differences with Simulated Wet (13%) Turbine Exhaust and 6 ppm Ammonia through Sample Conditioning Systems

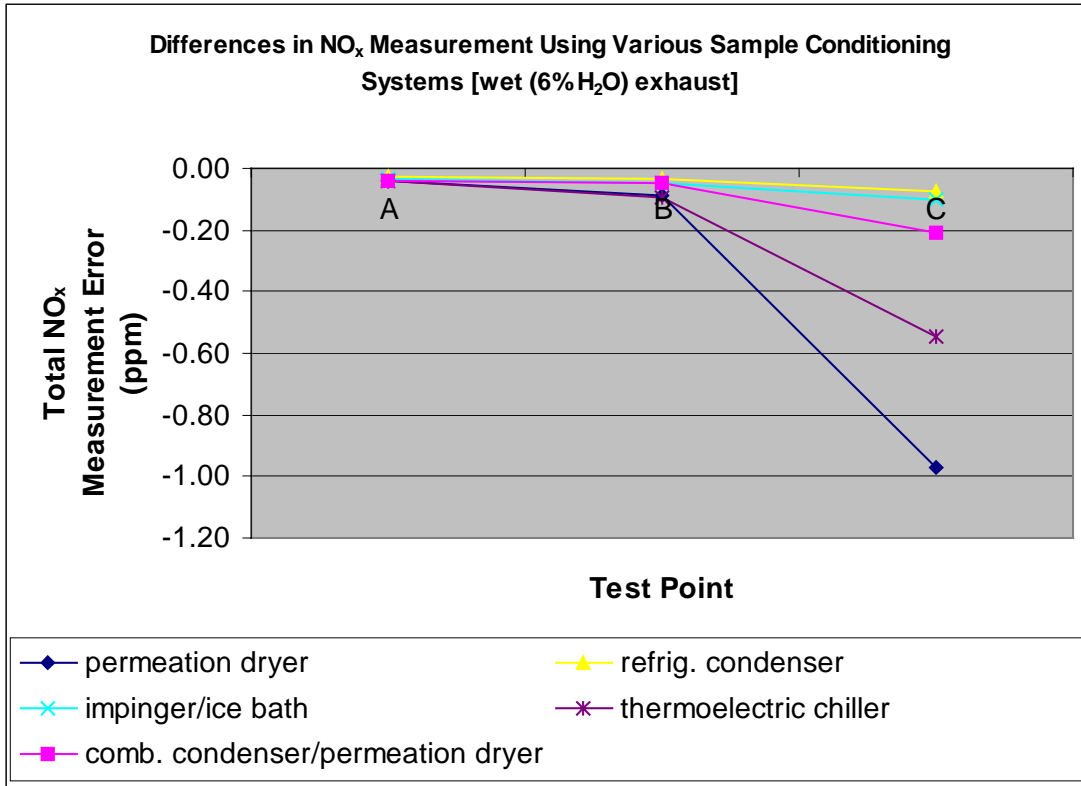


Simulated Exhaust Conditions	
Component	Concentration (dry basis)
CO ₂	4%
O ₂	15%
NH ₃	10 ppm

Moisture	13%
----------	-----

Test Point	Nominal NO (ppm)	Nominal NO ₂ (ppm)	Nominal NO _x (ppm)
A	0.00	0.00	0.00
B	0.20	0.20	0.40
C	5.00	5.00	10.00
D	0.00	0.00	0.00

Figure 9: NO_x Measurement Differences with Simulated Wet (13%) Turbine Exhaust and 10 ppm Ammonia through Sample Conditioning Systems

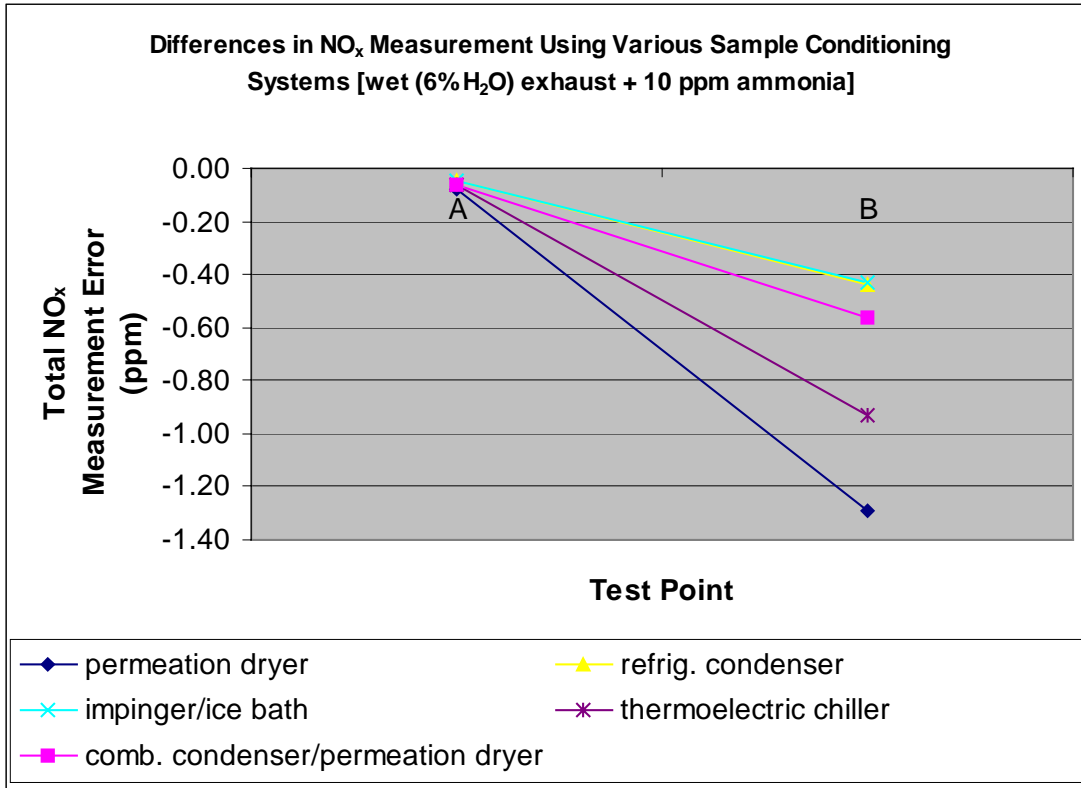


Simulated Exhaust Conditions	
Component	Concentration (dry basis)
CO ₂	4%
O ₂	15%
NH ₃	0 ppm

Moisture	6%
----------	----

Test Point	Nominal NO (ppm)	Nominal NO ₂ (ppm)	Nominal NO _x (ppm)
A	0.00	0.00	0.00
B	0.20	0.20	0.40
C	5.00	5.00	10.00

Figure 10: NO_x Measurement Differences with Simulated Wet (6%) Turbine Exhaust through Sample Conditioning Systems



Simulated Exhaust Conditions	
Component	Concentration (dry basis)
CO ₂	4%
O ₂	15%
NH ₃	10 ppm

Moisture	6%
----------	----

Test Point	Nominal NO (ppm)	Nominal NO ₂ (ppm)	Nominal NO _x (ppm)
A	0.20	0.20	0.40
B	5.00	5.00	10.00

Figure 11: NO_x Measurement Differences with Simulated Wet (6%) Turbine Exhaust with 10 ppm Ammonia through Sample Conditioning Systems.

Differences in measured NO_x values versus concentration inputs were evaluated for each of the sample conditioning methods under various simulated flue gas conditions.

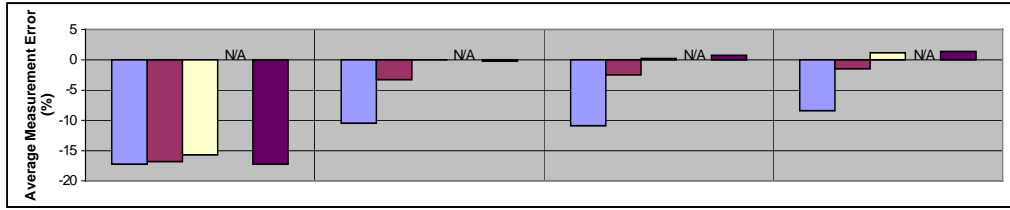
For simulated dry exhaust, overall average differences for all NO/NO₂ combinations ranged from -9.61 percent of input concentration (permeation dryer) to +8.70 percent (impingers in ice bath). For simulated wet exhaust (13 percent H₂O by volume), overall average differences for all NO/NO₂ combinations ranged from -10.8 percent of input concentration (permeation dryer) to +6.4 percent (refrigerated condenser). For simulated wet exhaust (13 percent H₂O by volume) with 6 ppmvd ammonia, overall average differences for all NO/NO₂ combinations ranged from -17.6 percent of input concentration (permeation dryer) to -4.0 percent (refrigerated condenser). For simulated wet exhaust (13 percent H₂O by volume) with 10 ppmvd ammonia, overall average differences for all NO/NO₂ combinations ranged from -17.2 percent of input concentration (permeation dryer) to -3.1 percent (impingers in an ice bath). For simulated partially wet exhaust (6 percent H₂O by volume), overall average differences for all NO/NO₂ combinations ranged from -13.2 percent of input concentration (permeation dryer) to +1.9 percent (impingers in an ice bath). For simulated partially wet exhaust (6 percent H₂O by volume) with 10 ppm ammonia, overall average differences for all NO/NO₂ combinations ranged from -12.3 percent of input concentration (permeation dryer) to +5.5 percent (refrigerated condenser).

Figure 12 presents the results in terms of percentage differences of measured values to inputted NO_x values for each test condition. Overall average differences ranged from -23 percent (for the 0.2/0.2 ppmd nominal NO/NO₂ input condition through the thermoelectric chiller) to +1 percent (for the 8.5/1.0 ppmd nominal NO/NO₂ condition through the refrigerated condenser).

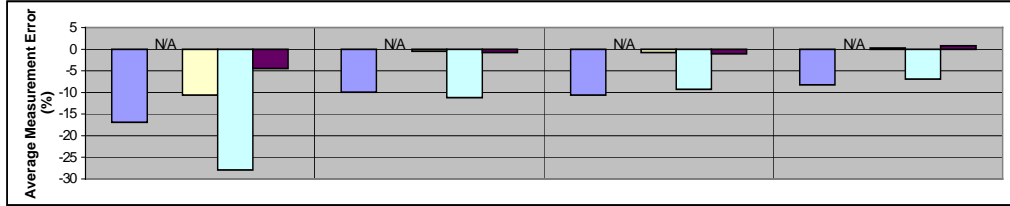
Most of the differences measured were negative, although there appears to be a slight positive bias in the refrigerated condenser and impingers in an ice bath at the higher NO_x input points. In general, the largest differences occurred at the test conditions with 13 percent H₂O and ammonia input. In general, the smallest differences occurred at the test conditions with dry simulated exhaust and no ammonia. The largest differences within any given test condition occurred at the lowest NO_x input points (0.2 ppmd NO and 0.2 ppmd NO₂), and in most cases was more than double the differences found at all other input concentrations.

Table 9 presents the precision of the tested systems at three different conditions. It is apparent from the table that precision is consistent for NO_x concentrations of 2 ppm and higher. Furthermore, the addition of water and ammonia to the sample stream do not appear to affect the precision of the tested systems.

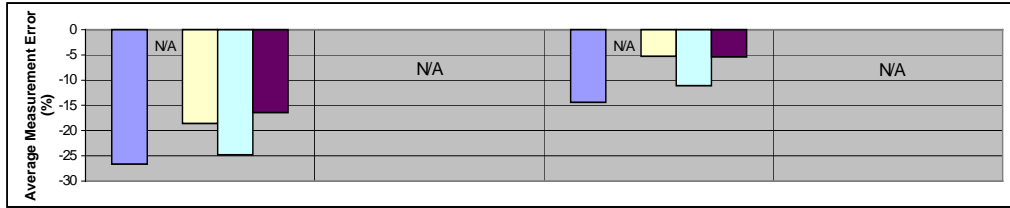
Dry Simulated Exhaust, no NH₃



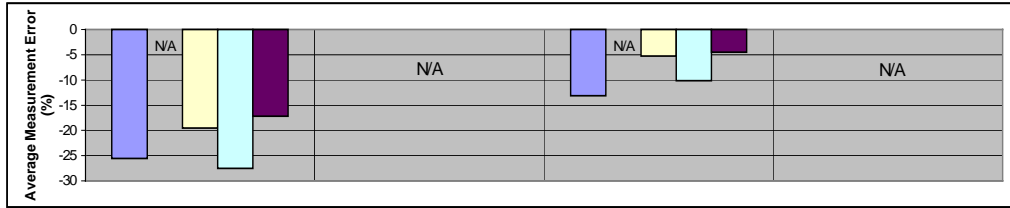
Wet (13% H₂O) Simulated Exhaust, no NH₃



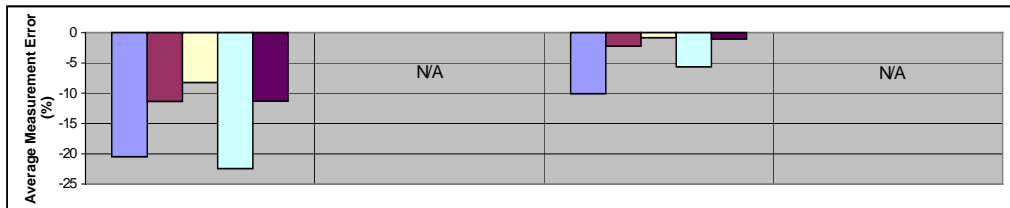
Wet (13% H₂O) Simulated Exhaust + 6 ppm NH₃



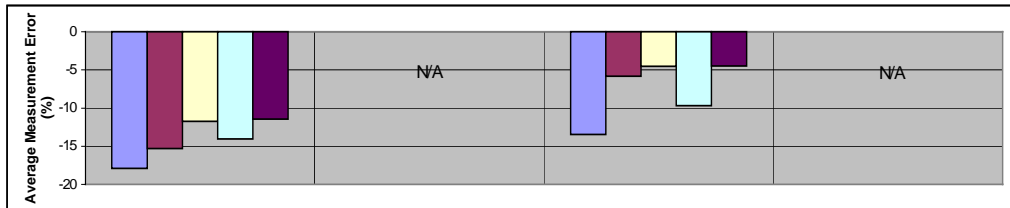
Wet (13% H₂O) Simulated Exhaust + 10 ppm NH₃



Wet (6% H₂O) Simulated Exhaust, no NH₃



Wet (6% H₂O) Simulated Exhaust + 10 ppm NH₃



Avg. Nominal NO Input (ppmd)	0.2	1	4.75	8.5
Avg. Nominal NO ₂ Input (ppmd)	0.2	1	4.75	1
Avg. Total NO _x Input (ppmd)	0.4	2	9.5	9.5

■ Permeation Dryer
■ Combination Ambient Condenser/Permeation Dryer
■ Refrigerated Condenser
■ Thermoelectric Chiller
■ Impingers in an Ice Bath

Figure 12: NO_x Measurement Differences using Various Sample Conditioning Systems

Table 9: Precision of NO_x Measurement through Various Sample Conditioning Systems

Condition: Dry Simulated Turbine Exhaust (15% O₂, 4% CO₂)

Avg. Nominal NO Input (ppmd)	0.2		1		4.75		8.5	
Avg. Nominal NO ₂ Input (ppmd)	0.2		1		4.75		1	
Avg. Total NO _x Input (ppmd)	0.4		2		9.5		9.5	
	Std. Dev.	SD/mean	Std. Dev.	SD/mean	Std. Dev.	SD/mean	Std. Dev.	SD/mean
Permeation Dryer	+/- 0.07 ppm	16.2%	+/- 0.13 ppm	6.4%	+/- 0.52 ppm	5.4%	+/- 0.52 ppm	5.5%
Combination Ambient Condenser/Perm	+/- 0.05 ppm	11.4%	+/- 0.13 ppm	6.4%	+/- 0.52 ppm	5.4%	+/- 0.46 ppm	4.8%
Refrigerated Condenser	+/- 0.05 ppm	11.0%	+/- 0.13 ppm	6.2%	+/- 0.49 ppm	5.2%	+/- 0.50 ppm	5.3%
Thermoelectric Chiller	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Glass Impingers in an Ice Bath	+/- 0.26 ppm	59.4%	+/- 0.19 ppm	9.2%	+/- 0.40 ppm	4.2%	+/- 0.42 ppm	4.4%

Condition: Wet Simulated Turbine Exhaust (13% H₂O, 13% O₂, 4% CO₂)

Avg. Nominal NO Input (ppmd)	0.2		1		4.75		8.5	
Avg. Nominal NO ₂ Input (ppmd)	0.2		1		4.75		1	
Avg. Total NO _x Input (ppmd)	0.4		2		9.5		9.5	
	Std. Dev.	SD/mean	Std. Dev.	SD/mean	Std. Dev.	SD/mean	Std. Dev.	SD/mean
Permeation Dryer	+/- 0.05 ppm	10.2%	+/- 0.13 ppm	6.4%	+/- 0.56 ppm	5.8%	+/- 0.56 ppm	5.9%
Combination Ambient Condenser/Perm	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Refrigerated Condenser	+/- 0.12 ppm	25.6%	+/- 0.15 ppm	7.2%	+/- 0.53 ppm	5.6%	+/- 0.52 ppm	5.5%
Thermoelectric Chiller	+/- 0.06 ppm	12.1%	+/- 0.14 ppm	6.6%	+/- 0.62 ppm	6.5%	+/- 0.62 ppm	6.6%
Glass Impingers in an Ice Bath	+/- 0.06 ppm	13.0%	+/- 0.11 ppm	5.2%	+/- 0.52 ppm	5.4%	+/- 0.50 ppm	5.2%

Condition: Wet Simulated Turbine Exhaust with Ammonia (13% H₂O, 13% O₂, 4% CO₂ + 10 ppm NH₃)

Avg. Nominal NO Input (ppmd)	0.2		1		4.75		8.5	
Avg. Nominal NO ₂ Input (ppmd)	0.2		1		4.75		1	
Avg. Total NO _x Input (ppmd)	0.4		2		9.5		9.5	
	Std. Dev.	SD/mean	Std. Dev.	SD/mean	Std. Dev.	SD/mean	Std. Dev.	SD/mean
Permeation Dryer	+/- 0.04 ppm	10.4%	N/A	N/A	+/- 0.56 ppm	5.8%	N/A	N/A
Combination Ambient Condenser/Perm	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Refrigerated Condenser	+/- 0.06 ppm	13.7%	N/A	N/A	+/- 0.54 ppm	5.6%	N/A	N/A
Thermoelectric Chiller	+/- 0.06 ppm	12.8%	N/A	N/A	+/- 0.62 ppm	6.5%	N/A	N/A
Glass Impingers in an Ice Bath	+/- 0.06 ppm	13.1%	N/A	N/A	+/- 0.54 ppm	5.7%	N/A	N/A

4.2.2 Evaluation of Heated Sampling Lines and Alternative Sampling Systems

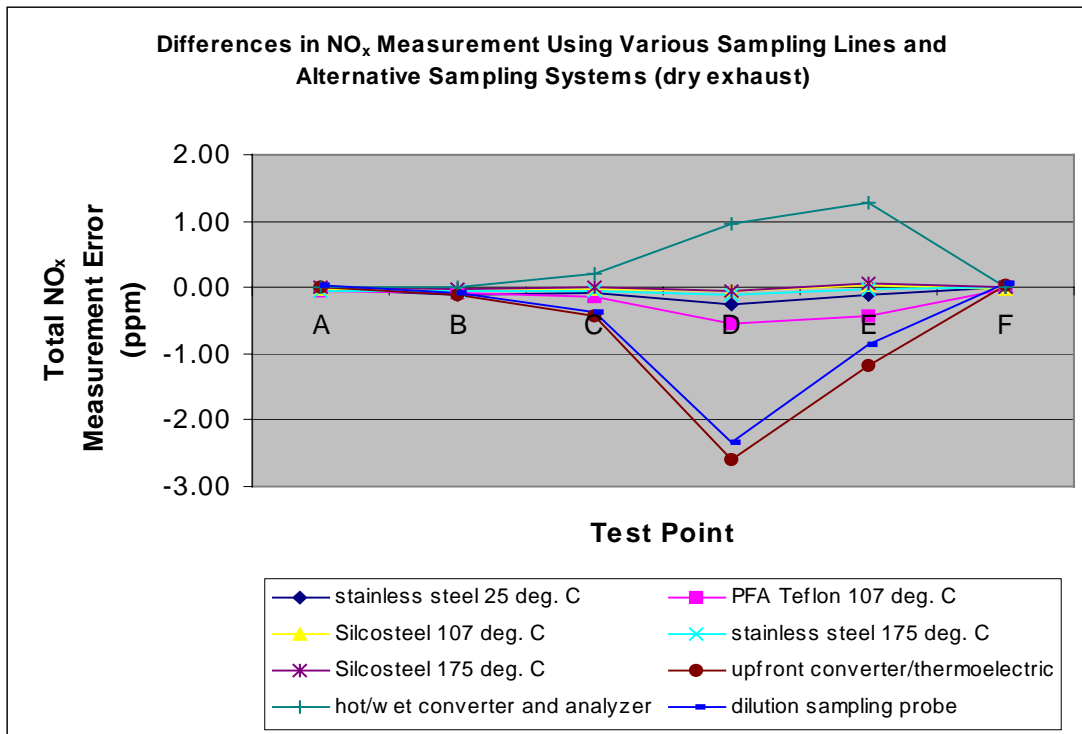
The thermoelectric chiller was chosen as the reference sample conditioner for this series of tests, which consisted of evaluation of various types of heated sample lines. The three specified lines were 100 feet long, made of Teflon, 316L stainless steel, and 316L Silcosteel®, respectively. They were hung in such a way as to eliminate any dips. Measurement differences using different sample lines were evaluated on a dry basis. Before testing, the analyzers were calibrated according to the procedures detailed in Section 4.1.1. The evaluation testing was conducted with the sample lines set at three temperatures: 25°C (ambient), 107°C, and 175°C. The outlet of each sample line was connected to the thermoelectric moisture removal system described in Section 4.1.3. The outlet of the moisture removal system was connected to the quartz sample gas manifold by means of a short length of PFA Teflon tubing. The manifold was connected to the NO_x analyzer with the molybdenum converter, chosen as the reference analyzer for these tests due to low response to ammonia and high converter efficiency.

In addition to the evaluating the sampling lines, this set of tests was used to concurrently evaluate three alternative sampling systems. The systems included a hot/wet system with a molybdate carbon converter (no moisture removal), a system with an upfront vitreous carbon converter and moisture removal system, and a dilution sampling probe with an unheated line

and molybdate carbon converter. Measurement differences for the hot/wet system and dilution extractive system were evaluated on a wet basis, and differences using the upfront converter were evaluated on a dry basis.

Each of the three sample lines was tested (at various temperatures) and the alternative systems were tested according to the nominal input concentration test matrix specified in Table 3 (note: the sample lines used with the dilution extractive probe were evaluated only at ambient temperatures, and the sample lines for the two alternative systems were evaluated at 107°C).

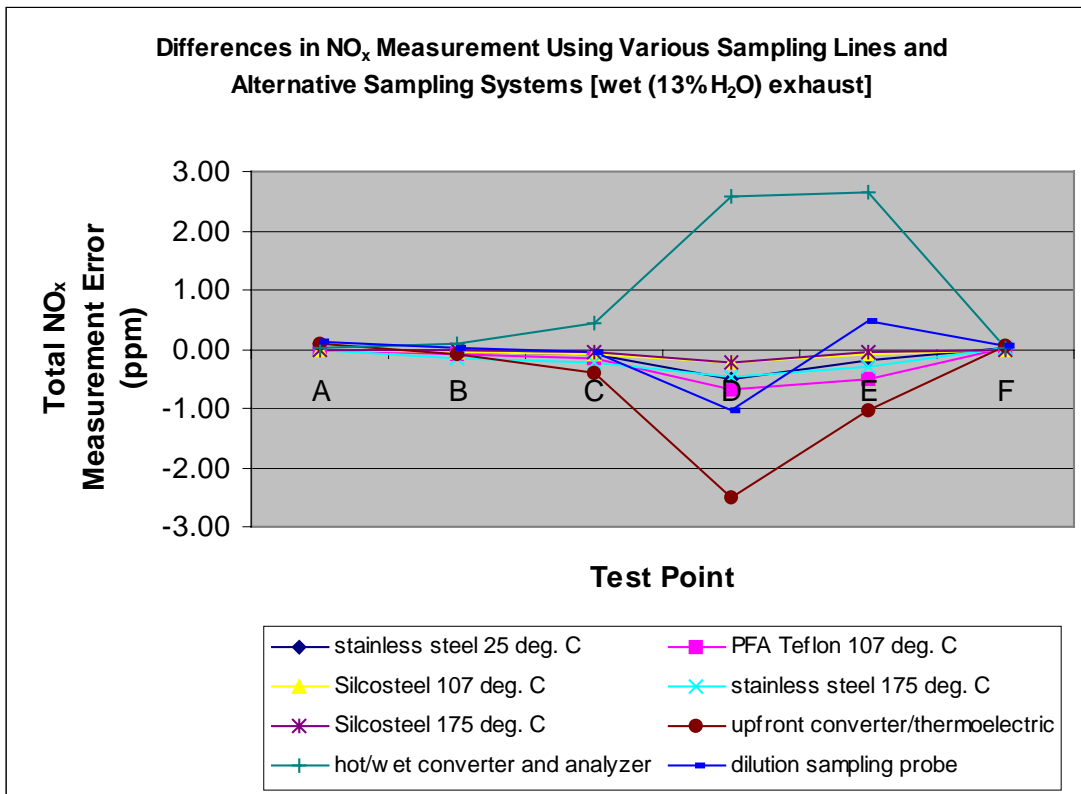
Figure 13, Figure 14, Figure 15, Figure 16, Figure 17, and Figure 18 present the results of testing using the various sample lines at different temperatures, and results from testing the alternative systems. In each figure, the results from all simultaneously operated sampling systems are presented.



Simulated Exhaust Conditions	
Component	Concentration (dry basis)
CO ₂	4%
O ₂	15%
NH ₃	0 ppm
Moisture	0%

Test Point	Nominal NO (ppm)	Nominal NO ₂ (ppm)	Nominal NO _x (ppm)
A	0.00	0.00	0.00
B	0.20	0.20	0.40
C	1.00	1.00	2.00
D	5.00	5.00	10.00
E	9.00	1.00	10.00
F	0.00	0.00	0.00

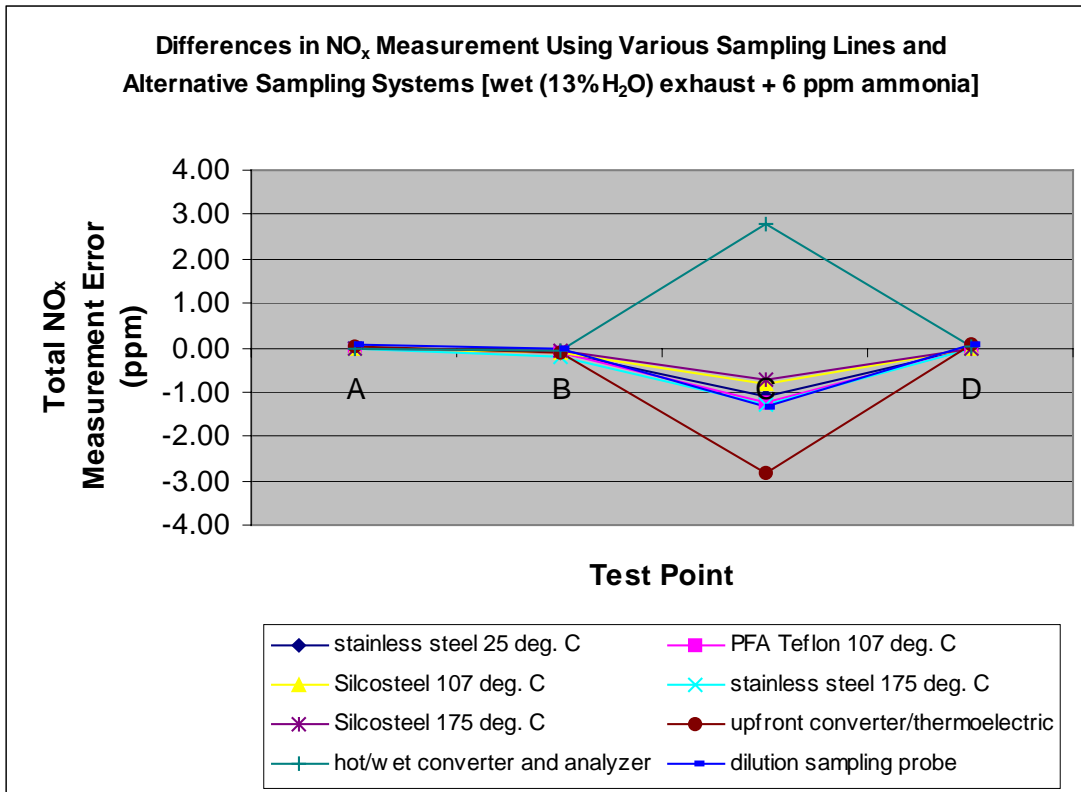
Figure 13: NO_x Measurement Differences with Simulated Dry Turbine Exhaust through Sample Lines and Alternative Sampling Systems.



Simulated Exhaust Conditions	
Component	Concentration (dry basis)
CO ₂	4%
O ₂	15%
NH ₃	0 ppm
Moisture	
	13%

Test Point	Nominal NO (ppm)	Nominal NO ₂ (ppm)	Nominal NO _x (ppm)
A	0.00	0.00	0.00
B	0.20	0.20	0.40
C	1.00	1.00	2.00
D	5.00	5.00	10.00
E	9.00	1.00	10.00
F	0.00	0.00	0.00

Figure 14: NO_x Measurement Differences with Simulated Wet (13%) Turbine Exhaust through Sample Lines and Alternative Sampling Systems

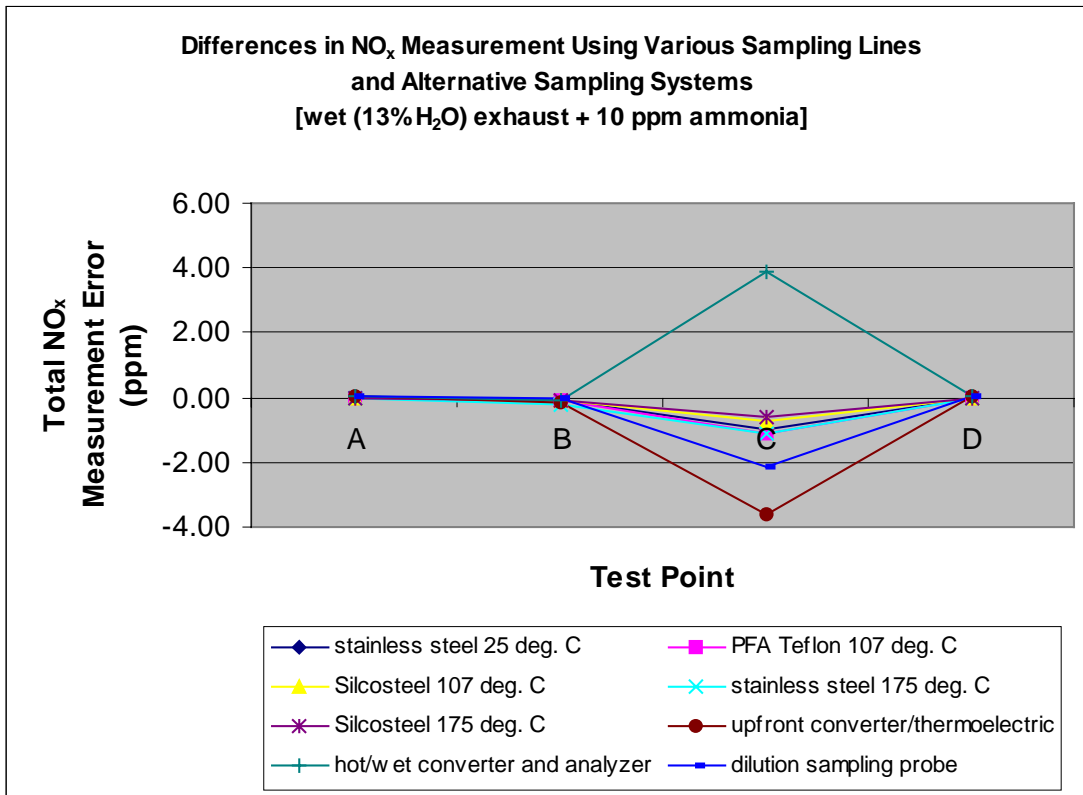


Simulated Exhaust Conditions	
Component	Concentration (dry basis)
CO ₂	4%
O ₂	15%
NH ₃	6 ppm

Moisture	13%
----------	-----

Test Point	Nominal NO (ppm)	Nominal NO ₂ (ppm)	Nominal NO _x (ppm)
A	0.00	0.00	0.00
B	0.20	0.20	0.40
C	5.00	5.00	10.00
D	0.00	0.00	0.00

Figure 15: NO_x Measurement Differences with Simulated Wet (13%) Turbine Exhaust and 6 ppm Ammonia through Sample Lines and Alternative Sampling Systems

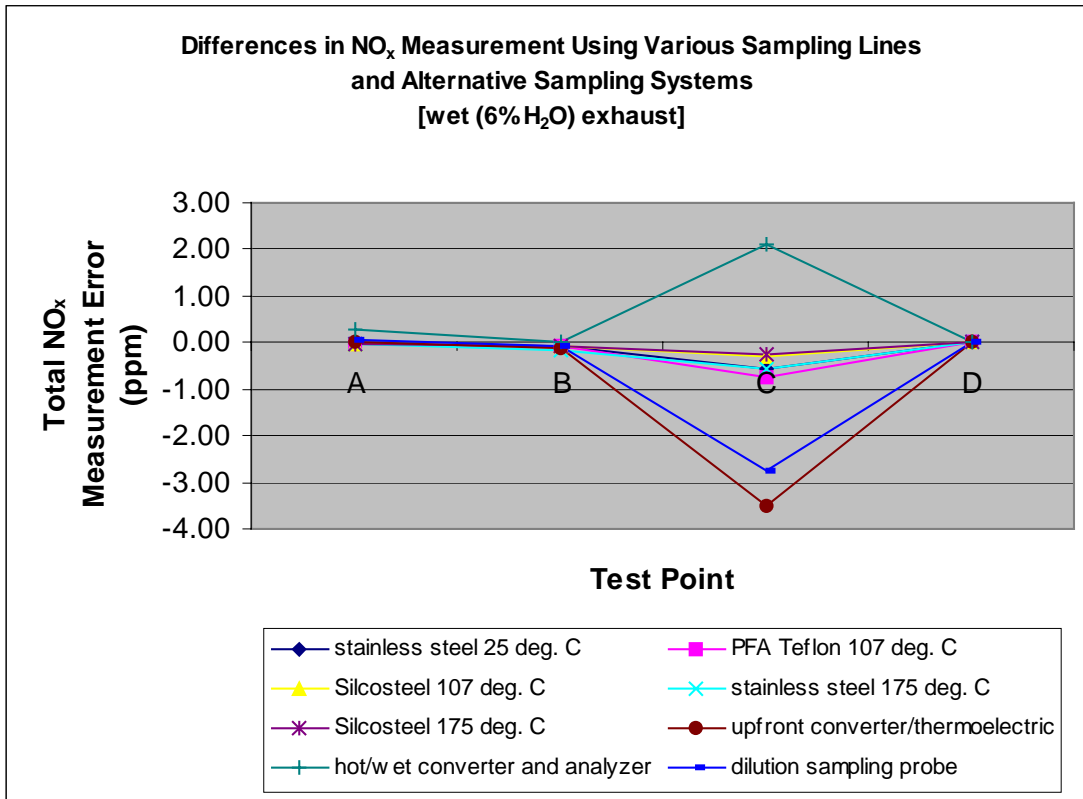


Simulated Exhaust Conditions	
Component	Concentration (dry basis)
CO ₂	4%
O ₂	15%
NH ₃	10 ppm

Moisture	13%
----------	-----

Test Point	Nominal NO (ppm)	Nominal NO ₂ (ppm)	Nominal NO _x (ppm)
A	0.00	0.00	0.00
B	0.20	0.20	0.40
C	5.00	5.00	10.00
D	0.00	0.00	0.00

Figure 16: NO_x Measurement Differences with Simulated Wet (13%) Turbine Exhaust and 10 ppm Ammonia through Sample Lines and Alternative Sampling Systems

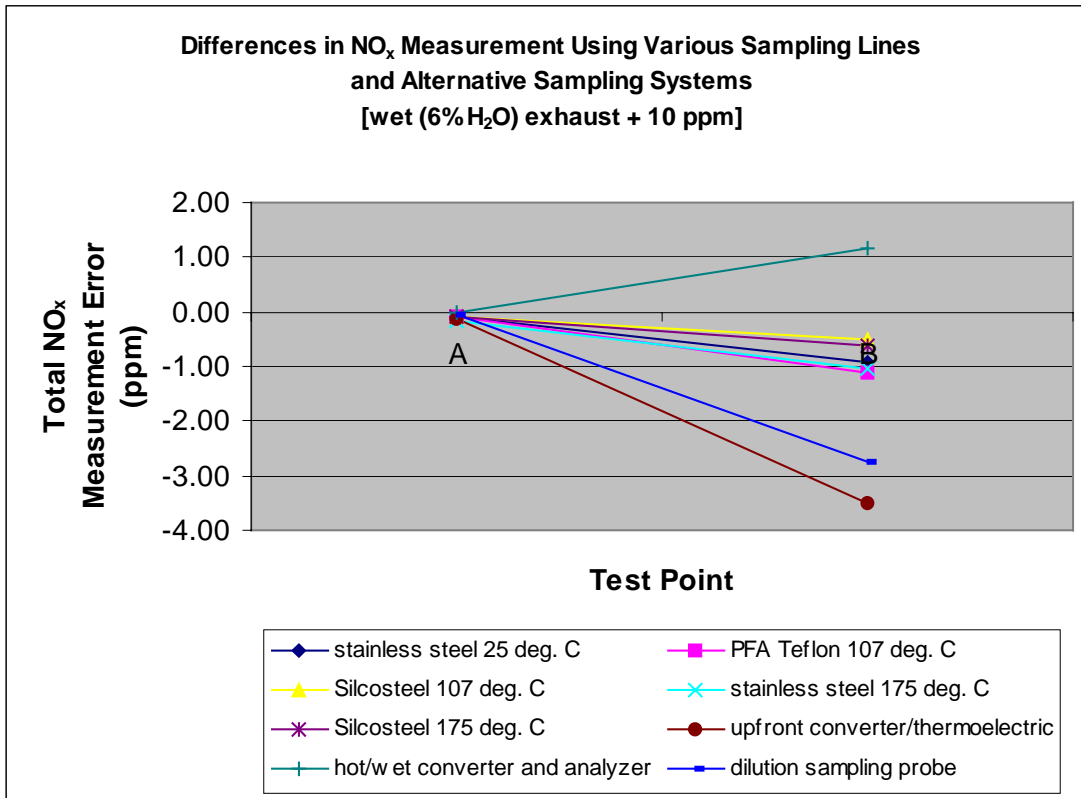


Simulated Exhaust Conditions	
Component	Concentration (dry basis)
CO ₂	4%
O ₂	15%
NH ₃	0 ppm

Moisture	6%
----------	----

Test Point	Nominal NO (ppm)	Nominal NO ₂ (ppm)	Nominal NO _x (ppm)
A	0.00	0.00	0.00
B	0.20	0.20	0.40
C	5.00	5.00	10.00
D	0.00	0.00	0.00

Figure 17: NO_x Measurement Differences with Simulated Wet (6%) Turbine Exhaust through Sample Lines and Alternative Sampling Systems



Simulated Exhaust Conditions	
Component	Concentration (dry basis)
CO ₂	4%
O ₂	15%
NH ₃	10 ppm

Moisture	6%
----------	----

Test Point	Nominal NO (ppm)	Nominal NO ₂ (ppm)	Nominal NO _x (ppm)
A	0.20	0.20	0.40
B	5.00	5.00	10.00

Figure 18: NO_x Measurement Differences with Simulated Wet (6%) Turbine Exhaust and 10 ppm Ammonia through Sample Lines and Alternative Sampling Systems

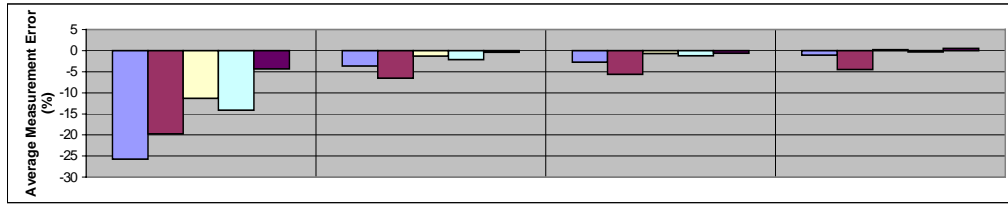
Differences in measured NO_x values versus concentration inputs were evaluated for each of the sample line materials and temperatures under various simulated flue gas conditions.

For simulated dry exhaust, overall average differences for all NO/NO₂ combinations ranged from -4.5 percent of input concentration (PFA Teflon at 107°C) to +7.7 percent (Silcosteel® at 175°C). For simulated wet exhaust (13 percent H₂O by volume), overall average differences for all NO/NO₂ combinations ranged from -7.4 percent of input concentration (stainless steel at 175°C) to +5.1 percent (Silcosteel® at 175°C). For simulated wet exhaust (13 percent H₂O by volume) with 6 ppmvd ammonia, overall average differences for all NO/NO₂ combinations ranged from -21.9 percent of input concentration (stainless steel at 175°C) to -5.9 percent (Silcosteel® at 175°C). For simulated wet exhaust (13 percent H₂O by volume) with 10 ppmvd ammonia, overall average differences for all NO/NO₂ combinations ranged from -22.6 percent of input concentration (stainless steel at 175°C) to -6.9 percent (Silcosteel® at 175°C).

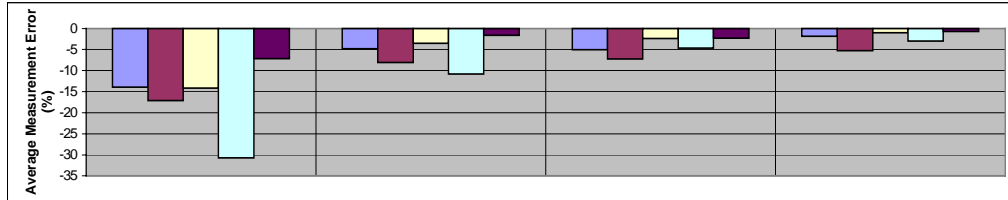
For simulated partially wet exhaust (6 percent H₂O by volume), overall average differences for all NO/NO₂ combinations ranged from -10.9 percent of input concentration (PFA Teflon at 107°C) to +0.9 percent (stainless steel at 25°C). For simulated partially wet exhaust (6 percent H₂O by volume) with 10 ppm ammonia, overall average differences for all NO/NO₂ combinations ranged from -13.5 percent of input concentration (stainless steel at 175°C) to -3.5 percent (Silcosteel® at 175°C).

Figure 19 and Figure 20 present the sample line testing results in terms of percentage differences of measured values to inputted NO_x values for each test condition (the alternative systems are discussed in the next section). Figure 19 shows results for each sample line test conducted with the reference sample conditioner (thermoelectric chiller). Figure 20 shows the same results adjusted for the measured thermoelectric chiller losses from the previous testing. Overall differences in the first case (sample lines + thermoelectric chiller) ranged from -37 percent (for the 0.2/0.2 ppmd nominal NO/NO₂ input condition through the stainless steel sampling line at 175°C + thermoelectric chiller) to 0 percent (for the 8.5/1.0 ppmd nominal NO/NO₂ condition through the Silcosteel® sampling line at both 107°C and 175°C + thermoelectric chiller). Overall differences in the second case (sample lines adjusted for thermoelectric chiller differences) ranged from -17 percent (for the 0.2/0.2 ppmd nominal NO/NO₂ input condition through the stainless steel sampling line at 175°C) to +11 percent (for the 1.0/1.0 ppmd nominal NO/NO₂ condition through the Silcosteel® sampling line at 175°C).

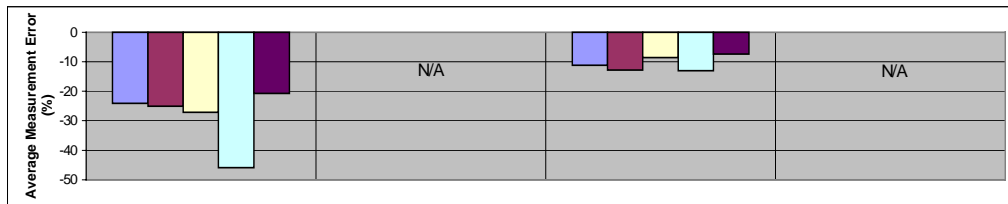
Dry Simulated Exhaust, no NH₃



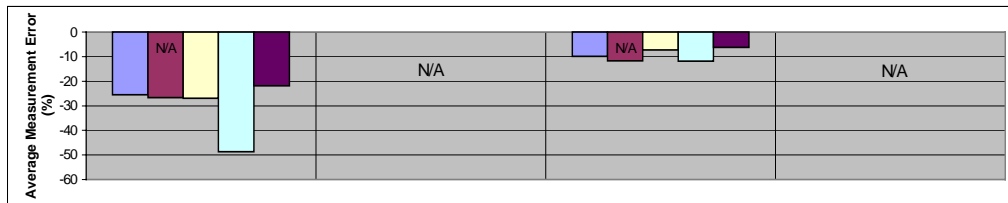
Wet (13% H₂O) Simulated Exhaust, no NH₃



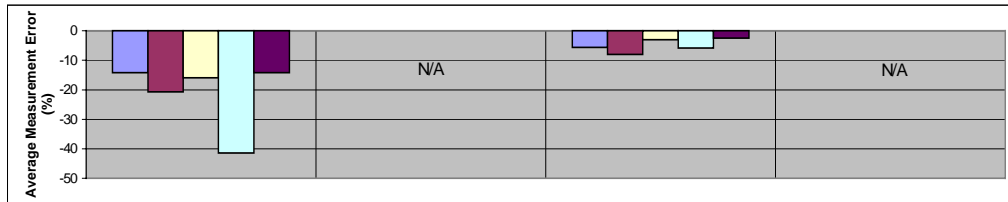
Wet (13% H₂O) Simulated Exhaust + 6 ppm NH₃



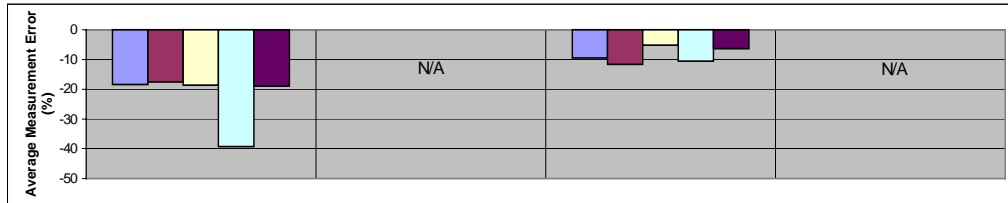
Wet (13% H₂O) Simulated Exhaust + 10 ppm NH₃



Wet (6% H₂O) Simulated Exhaust, no NH₃



Wet (6% H₂O) Simulated Exhaust + 10 ppm NH₃



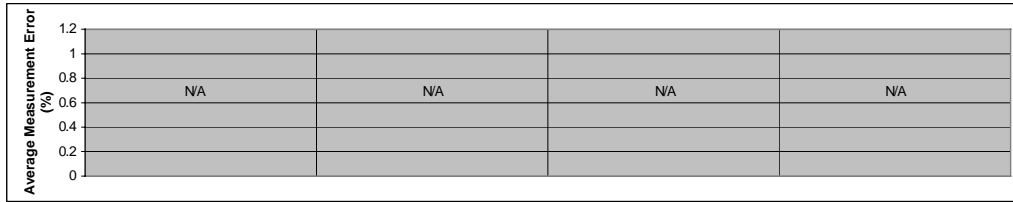
Avg. Nominal NO Input (ppmd)	0.2	1	4.75	8.5
Avg. Nominal NO ₂ Input (ppmd)	0.2	1	4.75	1
Avg. Total NO _x Input (ppmd)	0.4	2	9.5	9.5

■ 100 ft. Stainless Steel Sampling Line @ 25 °C
■ 100 ft. PFA Teflon Sampling Line @ 107 °C
■ 100 ft. Silcosteel™ Sampling Line @ 107 °C

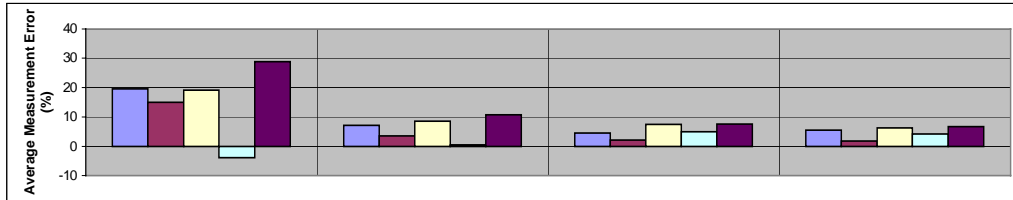
■ 100 ft. Stainless Steel Sampling Line @ 175 °C
■ 100 ft. Silcosteel™ Sampling Line @ 175 °C

Figure 19: NO_x Measurement Differences using Various Sample Lines and Materials through a Thermoelectric Chiller

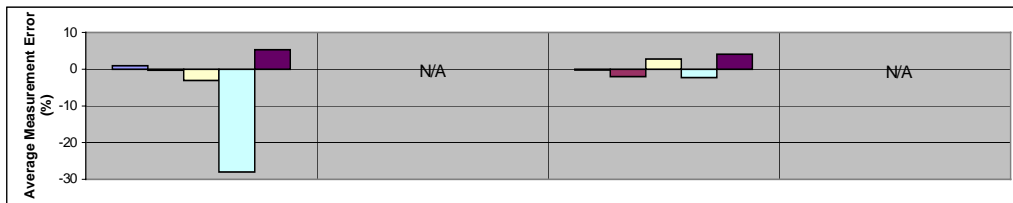
Dry Simulated Exhaust, no NH₃



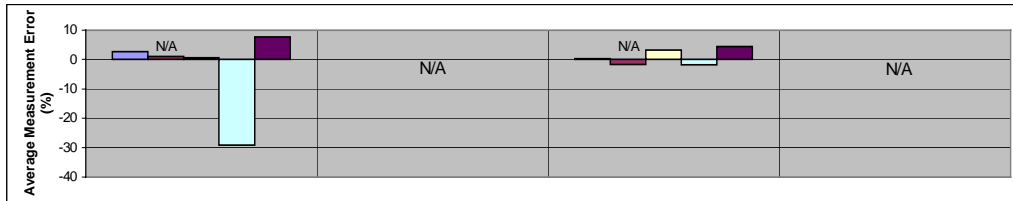
Wet (13% H₂O) Simulated Exhaust, no NH₃



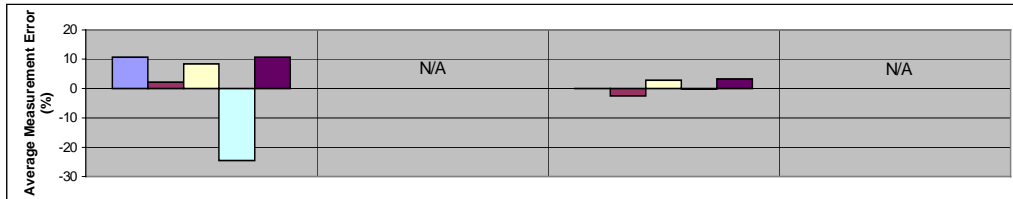
Wet (13% H₂O) Simulated Exhaust + 6 ppm NH₃



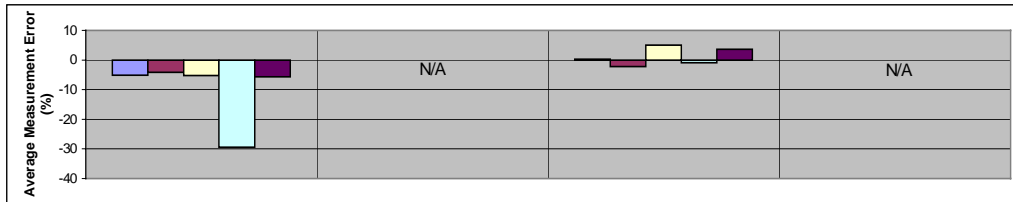
Wet (13% H₂O) Simulated Exhaust + 10 ppm NH₃



Wet (6% H₂O) Simulated Exhaust, no NH₃



Wet (6% H₂O) Simulated Exhaust + 10 ppm NH₃



Avg. Nominal NO Input (ppmd)	0.2	1	4.75	8.5
Avg. Nominal NO ₂ Input (ppmd)	0.2	1	4.75	1
Avg. Total NO _x Input (ppmd)	0.4	2	9.5	9.5

- 100 ft. Stainless Steel Sampling Line @ 25 °C
■ 100 ft. PFA Teflon Sampling Line @ 107 °C
■ 100 ft. Silcosteel™ Sampling Line @ 107 °C
- 100 ft. Stainless Steel Sampling Line @ 175 °C
■ 100 ft. Silcosteel™ Sampling Line @ 175 °C

Figure 20: NO_x Measurement Differences using Various Sample Lines and Materials (Corrected for Losses due to Thermoelectric Chiller)

Table 10 presents the precision of the tested sample lines (through the reference conditioner at three different conditions. As was the case with the sample conditioning systems, the precision is consistent for NO_x concentrations of 2 ppm and higher. Furthermore, the addition of water and ammonia to the sample stream do not appear to affect the precision of the tested sample line configurations.

Table 10: Precision of NO_x Measurement Through Various Sample Lines

Condition: Dry Simulated Turbine Exhaust (15% O₂, 4% CO₂)

Avg. Nominal NO Input (ppmd)	0.2		1		4.75		8.5	
Avg. Nominal NO ₂ Input (ppmd)	0.2		1		4.75		1	
Avg. Total NO _x Input (ppmd)	0.4		2		9.5		9.5	
	Std. Dev.	SD/mean	Std. Dev.	SD/mean	Std. Dev.	SD/mean	Std. Dev.	SD/mean
Stainless Steel Sample Line (25 °C)	+/- 0.07 ppm	16.8%	+/- 0.12 ppm	5.5%	+/- 0.50 ppm	5.1%	+/- 0.49 ppm	5.1%
Teflon Sample Line (107 °C)	+/- 0.11 ppm	26.3%	+/- 0.12 ppm	5.8%	+/- 0.42 ppm	4.2%	+/- 0.40 ppm	4.2%
SilcoSteel Sample Line (107 °C)	+/- 0.13 ppm	29.0%	+/- 0.16 ppm	7.3%	+/- 0.45 ppm	4.2%	+/- 0.41 ppm	4.2%
Stainless Steel Sample Line (175 °C)	+/- 0.06 ppm	13.6%	+/- 0.12 ppm	5.8%	+/- 0.46 ppm	4.6%	+/- 0.45 ppm	4.6%
SilcoSteel Sample Line (175 °C)	+/- 0.13 ppm	29.0%	+/- 0.14 ppm	6.8%	+/- 0.45 ppm	4.5%	+/- 0.44 ppm	4.5%

Condition: Wet Simulated Turbine Exhaust (13% H₂O, 13% O₂, 4% CO₂)

Avg. Nominal NO Input (ppmd)	0.2		1		4.75		8.5	
Avg. Nominal NO ₂ Input (ppmd)	0.2		1		4.75		1	
Avg. Total NO _x Input (ppmd)	0.4		2		9.5		9.5	
	Std. Dev.	SD/mean	Std. Dev.	SD/mean	Std. Dev.	SD/mean	Std. Dev.	SD/mean
Stainless Steel Sample Line (25 °C)	+/- 0.05 ppm	11.3%	+/- 0.11 ppm	5.0%	+/- 0.50 ppm	5.1%	+/- 0.49 ppm	5.1%
Teflon Sample Line (107 °C)	+/- 0.04 ppm	9.0%	+/- 0.09 ppm	4.3%	+/- 0.47 ppm	4.9%	+/- 0.46 ppm	4.8%
SilcoSteel Sample Line (107 °C)	+/- 0.08 ppm	17.2%	+/- 0.12 ppm	5.8%	+/- 0.52 ppm	5.4%	+/- 0.47 ppm	4.9%
Stainless Steel Sample Line (175 °C)	+/- 0.07 ppm	13.6%	+/- 0.09 ppm	4.1%	+/- 0.47 ppm	4.9%	+/- 0.52 ppm	5.3%
SilcoSteel Sample Line (175 °C)	+/- 0.12 ppm	24.0%	+/- 0.10 ppm	4.7%	+/- 0.50 ppm	5.2%	+/- 0.45 ppm	4.6%

Condition: Wet Simulated Turbine Exhaust with Ammonia (13% H₂O, 13% O₂, 4% CO₂ + 10 ppm NH₃)

Avg. Nominal NO Input (ppmd)	0.2		1		4.75		8.5	
Avg. Nominal NO ₂ Input (ppmd)	0.2		1		4.75		1	
Avg. Total NO _x Input (ppmd)	0.4		2		9.5		9.5	
	Std. Dev.	SD/mean	Std. Dev.	SD/mean	Std. Dev.	SD/mean	Std. Dev.	SD/mean
Stainless Steel Sample Line (25 °C)	+/- 0.04 ppm	9.9%	N/A	N/A	+/- 0.48 ppm	4.9%	N/A	N/A
Teflon Sample Line (107 °C)	+/- 0.03 ppm	7.8%	N/A	N/A	+/- 0.48 ppm	5.0%	N/A	N/A
SilcoSteel Sample Line (107 °C)	+/- 0.05 ppm	11.1%	N/A	N/A	+/- 0.49 ppm	5.1%	N/A	N/A
Stainless Steel Sample Line (175 °C)	+/- 0.06 ppm	13.0%	N/A	N/A	+/- 0.48 ppm	5.0%	N/A	N/A
SilcoSteel Sample Line (175 °C)	+/- 0.05 ppm	11.8%	N/A	N/A	+/- 0.48 ppm	5.0%	N/A	N/A

An analysis of NO₂ recovery throughout the course of the test program was performed using direct NO₂ measurements from the luminol PAN gas chromatograph (LUM) and tunable diode laser (TDL) systems. These instruments were connected to the sample gas mixing system through a dilution sampling probe. The purpose of these tests was to determine the effects of water and ammonia on NO₂ conveyance through a sampling system. There were errors in the calibration of these instruments, and therefore the absolute recovery of NO₂ at any given test condition could not be determined. A relative comparison of the NO₂ recovery at each test condition, however, was performed. Figure 21 shows the relative percentage recovery (as measured by the luminol and TDL instruments) of NO₂ at each test condition as a function of NO₂ input concentration (as determined by mass flow controller set points). Measurements made by both instruments were highly variable, with standard deviations ranging from 10

percent to 200 percent of measured values. It is uncertain whether the variability is a function of actual sample composition variability or instrument error, but the data indicate a high degree of NO₂ concentration variability. In general, the TDL measurements showed a higher degree of NO₂ recovery than the luminol measurements.

Both instrumental measurements suggest a lower percentage recovery of NO₂ at the lowest input range (0.2 ppm input) than the higher concentration inputs. The TDL measurements indicate a reduction in NO₂ recovery with the addition of 13 percent water (compared with the dry gas condition), but the luminol measurements do not. The negative bias of TDL measurements was not seen, however, with the addition of six percent water. There were no statistically significant trends observed with the addition of ammonia to the sample stream for either instrument.

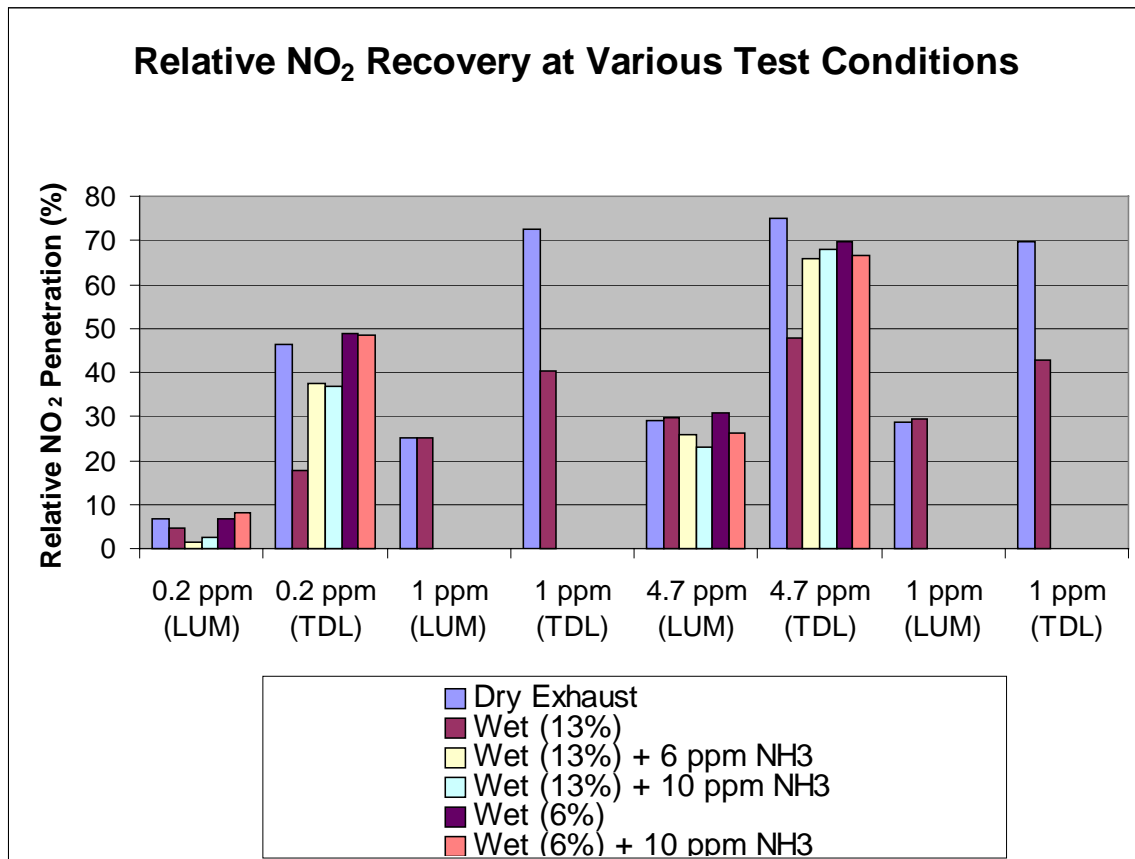


Figure 21: Relative NO₂ Recovery at Various Test Conditions

4.2.3 Alternative Sampling Systems

Differences in measured NO_x values versus concentration inputs were evaluated for each of the alternative sampling systems under various simulated flue gas conditions.

For simulated dry exhaust, overall average differences for all NO/NO₂ combinations ranged from -19.3 percent of input concentration (up-front converter) to +11.2 percent (hot/wet). For

simulated wet exhaust (13 percent H₂O by volume), overall average differences for all NO/NO₂ combinations ranged from -17.8 percent of input concentration (upfront converter) to +29.9 percent (hot/wet). For simulated wet exhaust (13 percent H₂O by volume) with 6 ppmvd ammonia, overall average differences for all NO/NO₂ combinations ranged from -28.1 percent of input concentration (upfront converter) to +30.8 percent (hot/wet). For simulated wet exhaust (13 percent H₂O by volume) with 10 ppmvd ammonia, overall average differences for all NO/NO₂ combinations ranged from -36.4 percent of input concentration (upfront converter) to +43.1 percent (hot/wet). For simulated partially wet exhaust (6 percent H₂O by volume), overall average differences for all NO/NO₂ combinations ranged from -35.4 percent of input concentration (upfront converter) to +25.2 percent (hot/wet). For simulated partially wet exhaust (6 percent H₂O by volume) with 10 ppm ammonia, overall average differences for all NO/NO₂ combinations ranged from -36.2 percent of input concentration (upfront converter) to +12.1 percent (hot/wet).

Figure 22 presents the results in terms of percentage differences of measured values to inputted NO_x values for each test condition. Overall average differences ranged from -31 percent (for the 4.7/4.7 ppmd nominal NO/NO₂ input condition through the analyzer with the vitreous carbon converter) to +26 percent (for the 4.7/4.7 ppmd nominal NO/NO₂ condition through the analyzer with the hot/wet molybdenum converter).

4.2.4 Additional Evaluation of Ammonia Effects

The initial NO_x measurement evaluations with added ammonia gave unexpected and seemingly inconsistent results. Additional testing was performed to more conclusively determine potential problems in measuring NO_x and NH₃. To evaluate the penetration of ammonia through sample conditioners and lines, synthetically prepared mixtures were again analyzed by chemiluminescent analyzers with and without these components installed. Measured ammonia was determined by the difference in measurements between a chemiluminescent analyzer equipped with a high temperature stainless steel converter and a chemiluminescent NO_x analyzer with a standard temperature stainless steel converter. The following describes the results of the additional testing.

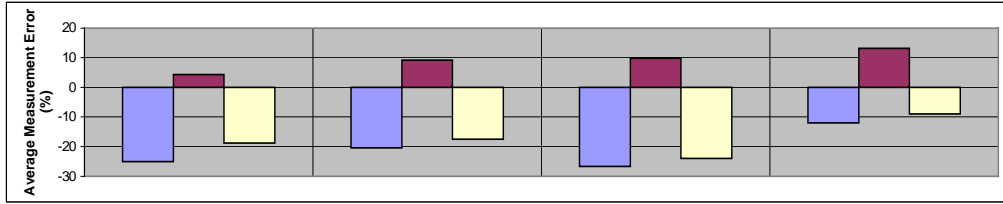
NH₃ Only in N₂/O₂

Test 1a- Refrigerated condenser (with minimal sample line length)

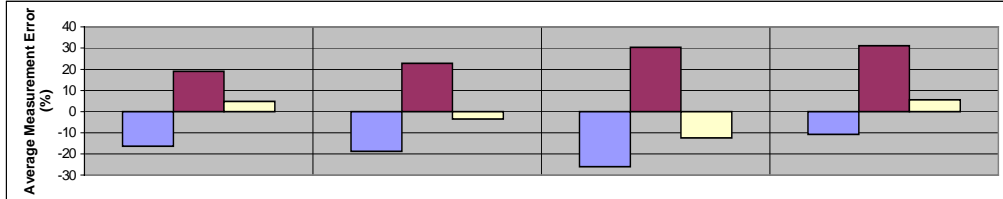
Figure 23 summarizes the results from this test using a refrigerated condenser. In dry air the measured ammonia is 91 percent of that calculated. When 13 percent water is added, the ammonia measured drops to 78 percent of the calculated amount. These values drop to 88 percent and 74 percent if the background (before ammonia was added) response of the NH₃ analyzer is subtracted. For this and all succeeding background corrections, we used this initial background since the analyzer appeared to take a considerable amount of time to reach a stable zero after ammonia was added to the system. The NO_x analyzer with the stainless steel converter responded significantly to the ammonia while the other two analyzer/converters did not. At both test points where ammonia was added (with and without water), the analyzer with the stainless steel converter exceeded the maximum analytical range (> 10 ppmd). There was

also a residual ammonia effect in the sampling systems as evidenced by the last two points (with 0 ppm NH₃ input) measured by both the NO_x analyzer with the stainless steel converter and to a lesser degree by the ammonia analyzer with the high temperature stainless steel converter.

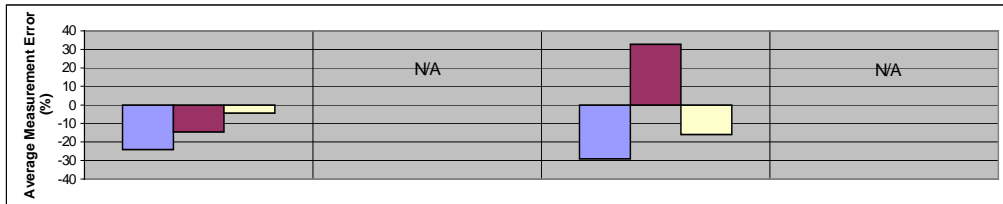
Dry Simulated Exhaust, no NH₃



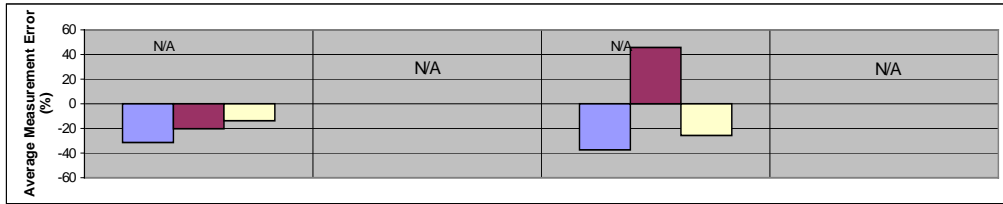
Wet (13% H₂O) Simulated Exhaust, no NH₃



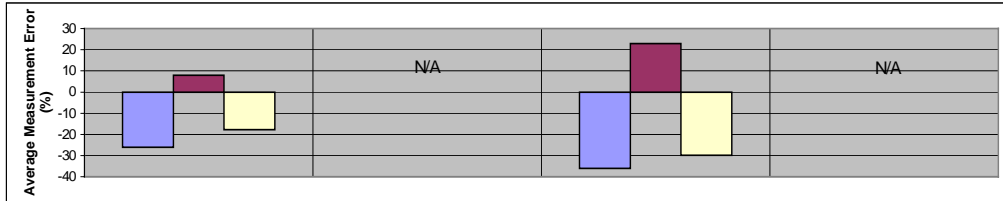
Wet (13% H₂O) Simulated Exhaust + 6 ppm NH₃



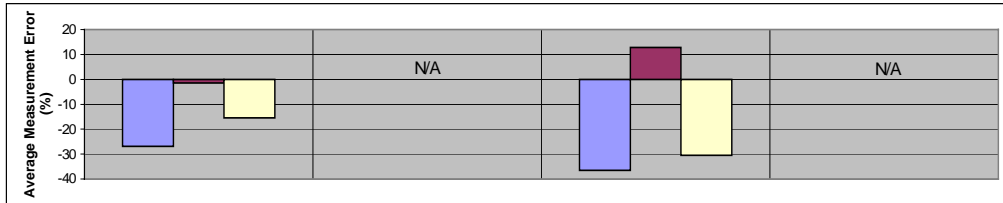
Wet (13% H₂O) Simulated Exhaust + 10 ppm NH₃



Wet (6% H₂O) Simulated Exhaust, no NH₃



Wet (6% H₂O) Simulated Exhaust + 10 ppm NH₃



Avg. Nominal NO Input (ppmd)	0.2	1	4.75	8.5
Avg. Nominal NO ₂ Input (ppmd)	0.2	1	4.75	1
Avg. Total NO _x Input (ppmd)	0.4	2	9.5	9.5

■ NO_x Analyzer with Hot/Wet Vitrous Carbon Converter and Thermoelectric Chiller
■ NO_x Analyzer with Hot/Wet Molybdate Carbon Converter
■ NO_x Analyzer with Dilution Extraction Probe

Figure 22: NO_x Measurement Errors using Various Alternative Sampling Systems

			SS	MOLY	MOLYC	NH ₃
Test Point	Input NH ₃ (ppmd)	Input H ₂ O % @ 191 °C	Measured NO _x (ppmd)	Measured NO _x (ppmd)	Measured NO _x (ppmd)	Measured NH ₃ (ppmd)
A	0.00	0.00	0.87	-0.04	0.04	0.48
B	14.92	0.00	10.12	-0.04	0.11	13.56
C	12.99	12.97	10.12	-0.05	0.11	10.13
D	0.00	13.02	2.30	-0.05	0.06	0.46
E	0.00	0.00	1.40	-0.05	0.05	0.28

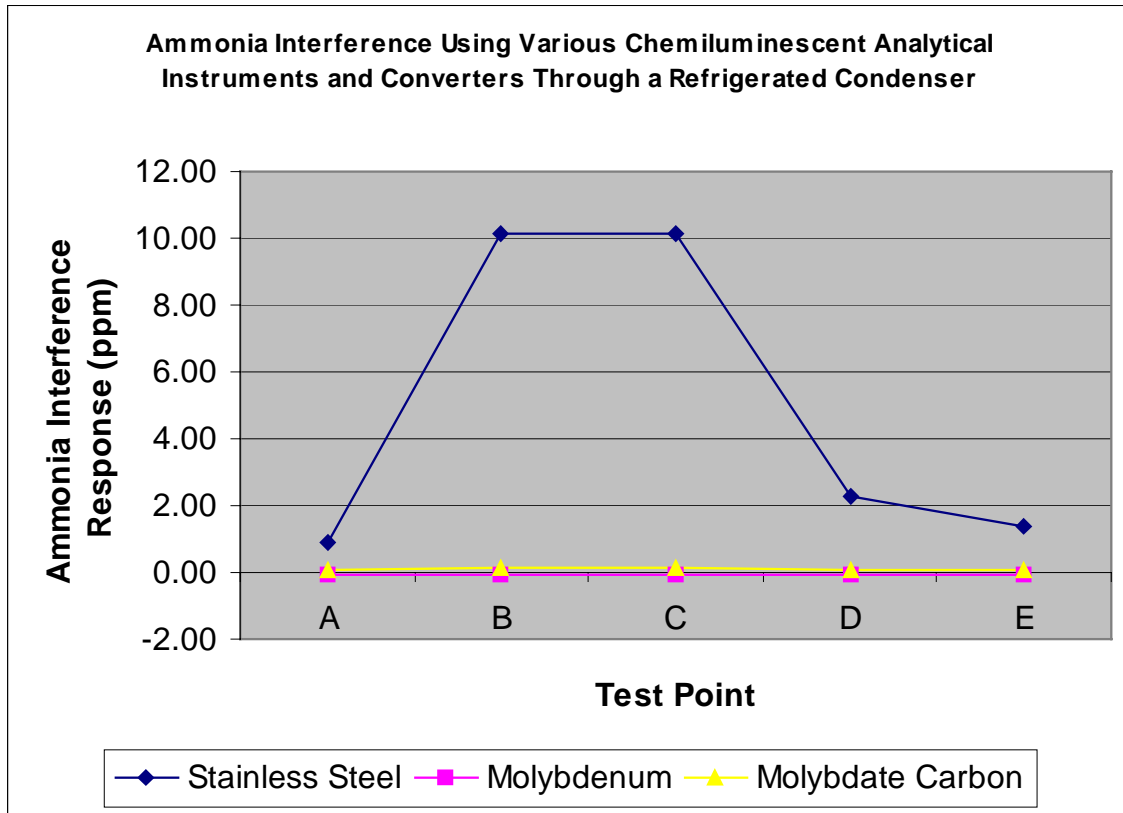


Figure 23: Refrigerated Condenser, Ammonia and Water Only

Test 2a- Impingers in an ice bath (with minimal sample line length)

Figure 24 summarizes the results from this test using glass impingers placed in an ice bath. The response of the ammonia analyzer for these tests is far lower than the previous one. Corrected for background, the ammonia response was 53 percent without added water and 59 percent with added water. The NO_x analyzer with the stainless steel converter is the only one that responds significantly to ammonia. Using the ammonia analyzer as the reference, the response was 82 percent with 6 percent added water and 96 percent with 13 percent added water. As above, there was a residual ammonia effect in the sampling systems as evidenced by the last point (with 0 ppm NH₃ input) measured by both the NO_x analyzer with the stainless steel converter and to a lesser degree by the ammonia analyzer.

			SS	MOLY	MOLYC	NH ₃
Test Point	Input NH ₃ (ppmd)	Input H ₂ O % @ 191 °C	Measured NO _x (ppm)	Measured NO _x (ppm)	Measured NO _x (ppm)	Measured NH ₃ (ppm)
A	0.00	0.00	0.83	-0.04	0.09	0.10
B	14.92	5.74	7.31	-0.05	0.08	8.03
C	12.99	12.97	8.12	-0.05	0.08	7.73
D	0.00	13.02	2.90	-0.05	0.06	1.32

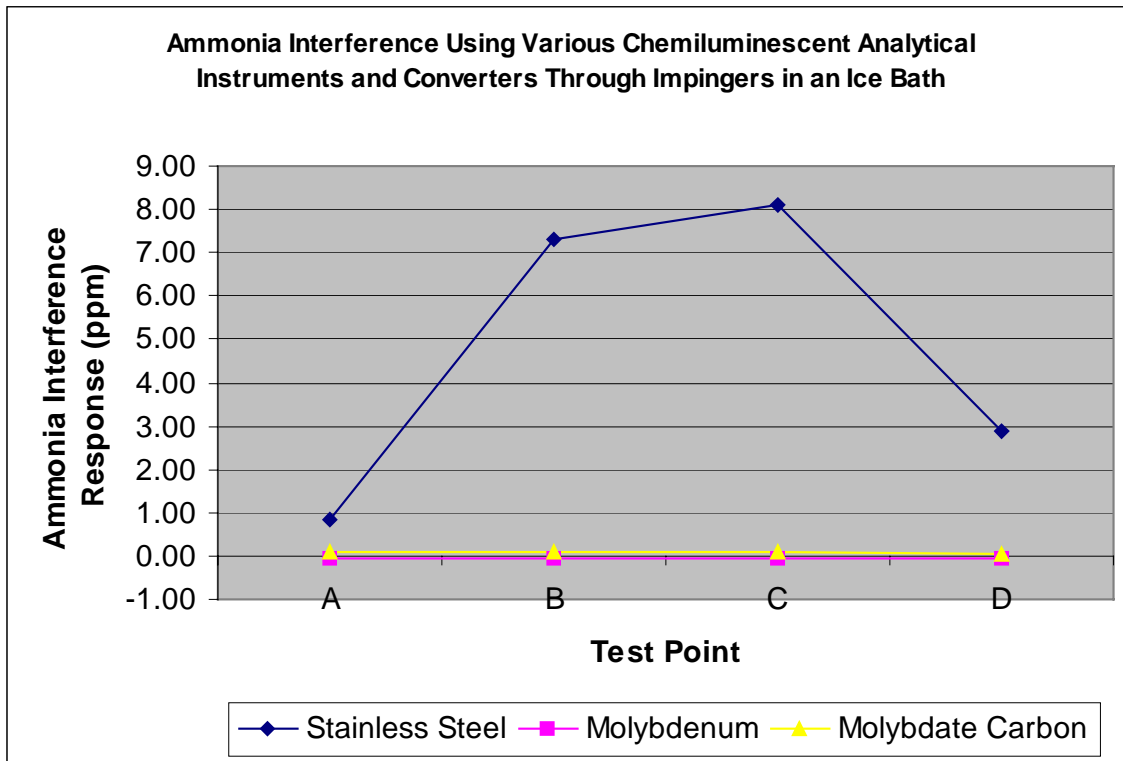


Figure 24: Impingers in an Ice Bath, Ammonia and Water Only

Test 3a- Thermoelectric chiller (with minimal sample line length)

Figure 25 summarizes the results from this test using a thermoelectric chiller for water removal. The response of the ammonia analyzer for these tests is similar to Test 1a. Corrected for background the ammonia response was 83 percent without added water, 87 percent with 6 percent added water and 91 percent with 13 percent added water. The NO_x analyzer with the stainless steel converter is again the only one that responds significantly to ammonia. As was the case in Test 1a, the test points where ammonia was added (with and without water), the analyzer with the stainless steel converter exceeded the maximum analytical range (> 10 ppmd). Once again, the third, fourth, and last two points demonstrated a residual (and repeatable) ammonia concentration measured by the NO_x analyzer/stainless steel converter and ammonia analyzer.

Test Point	Input NH ₃ (ppmd)	Input H ₂ O % @ 191 °C	SS	MOLY	MOLYC	NH ₃
			Measured NO _x (ppmd)	Measured NO _x (ppmd)	Measured NO _x (ppmd)	Measured NH ₃ (ppmd)
A	14.92	0.00	10.12	-0.04	0.16	12.48
B	14.06	5.74	10.12	-0.05	0.13	12.38
C	0.00	5.77	2.04	-0.05	0.07	0.40
D	0.00	0.00	0.86	-0.05	0.05	0.20
E	14.92	0.00	10.12	-0.05	0.14	13.16
F	12.99	12.97	10.12	-0.05	0.14	11.95
G	0.00	13.02	2.06	-0.05	0.07	0.36
H	0.00	0.00	1.01	-0.05	0.06	0.16

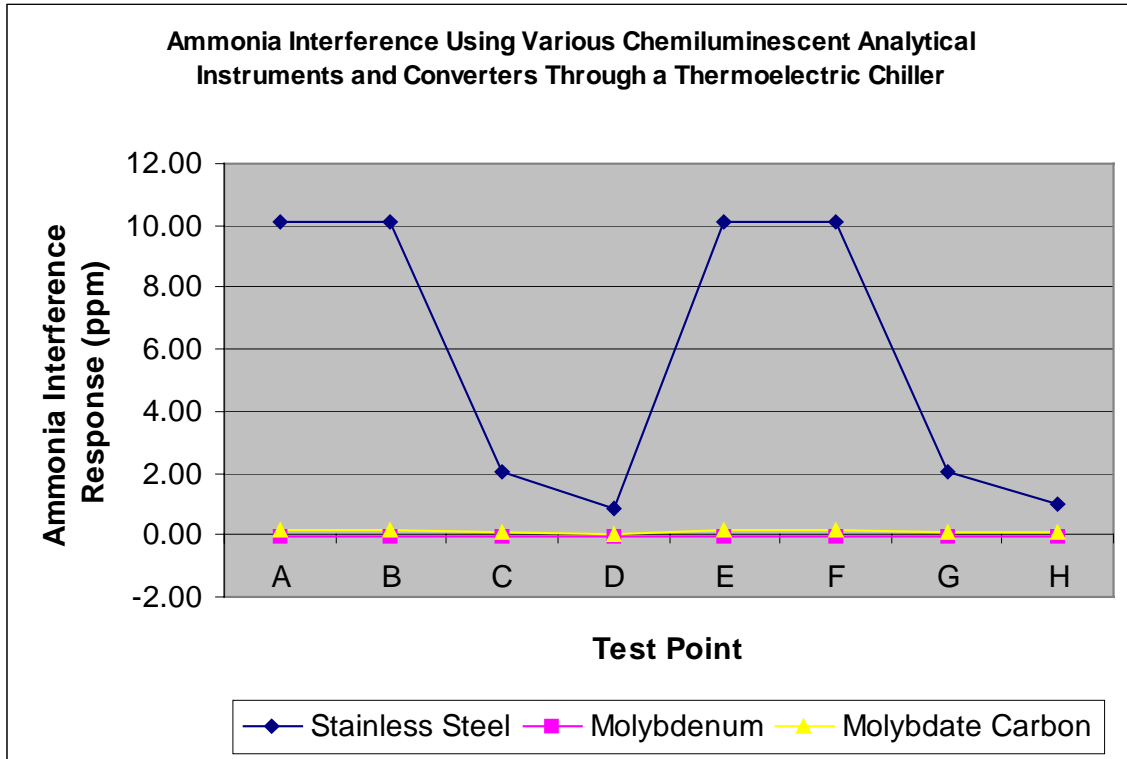


Figure 25: Thermoelectric Chiller, Ammonia and Water Only

Test 4a- Thermoelectric chiller with PFA sample line

This is similar to Test 3a but with the minimum length heated PFA Teflon transfer line replaced with a 100 ft. heated/unheated PFA sample line. Figure 26 summarizes the results. Ammonia was measured with an efficiency varying from 67 to 80 percent compared with that calculated. The NO_x analyzer with the stainless steel converter was again the only one to respond to ammonia. The response of the NO_x/stainless steel converter in all cases where ammonia was input was above the analytical range (>10 ppm). The measured ammonia concentration changed very little for dry gas with the sample line at room temperature and for ammonia with water added at temperature from 25°C to 175°C. We conclude that heating the sample line had no effect on ammonia penetration through the sampling line. The reason may be that the

ammonia vapor was in equilibrium with the liquid water that undoubtedly condensed in the sampling line.

Test Point	Temp. (°C)	Input NH ₃ (ppmd)	Input H ₂ O % @ 191 °C	SS	MOLY	MOLYC	NH ₃
				Measured NO _x (ppmd)	Measured NO _x (ppmd)	Measured NO _x (ppmd)	Measured NH ₃ (ppmd)
A	25.0	0.00	0.00	0.08	-0.05	0.10	0.02
B	25.0	14.92	0.00	10.12	0.01	0.22	10.02
C	25.0	12.99	12.97	10.12	-0.05	0.18	9.93
D	107.0	12.99	12.97	10.12	-0.05	0.19	10.56
E	175.0	12.99	12.97	10.12	-0.05	0.24	8.85

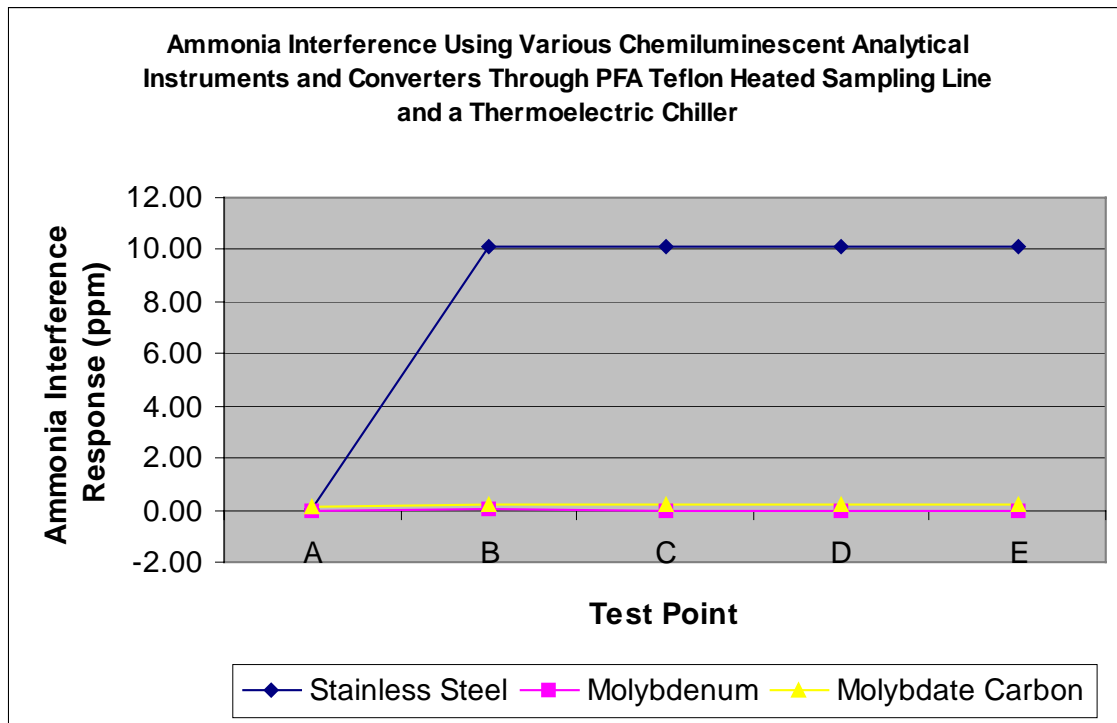


Figure 26: PFA Teflon sample Line through Thermoelectric Chiller, Ammonia and Water Only

Test 5a- Thermoelectric chiller with Silcosteel® sampling line

This is similar to Test 4a but with a 100 ft. Silcosteel® sample line instead of PFA. Figure 27 summarizes the results. Ammonia was measured with efficiencies varying from 77 to 81 percent compared with that calculated. The NO_x analyzer with the stainless steel converter was again the only one to respond to ammonia. The response of the NO_x/stainless steel converter in all cases where ammonia was input was above the analytical range (>10 ppm). The measured ammonia concentration changed very little for gas with water added as the temperature of the sampling line was increased from 25 to 175 °C. As with the PFA line, we conclude that heating the sample line had no effect on ammonia penetration through the sampling line.

Test Point	Temp. (°C)	Input NH ₃ (ppmd)	Input H ₂ O % @ 191°C	SS	MOLY	MOLYC	NH ₃
				Measured NO _x (ppmd)	Measured NO _x (ppmd)	Measured NO _x (ppmd)	Input NH ₃ (ppmd)
A	25.0	0.00	0.00	0.06	-0.05	0.00	0.02
B	25.0	12.99	12.97	10.12	-0.05	0.17	10.76
C	107.0	12.99	12.97	10.12	-0.05	0.16	10.15
D	175.0	12.99	12.97	10.12	-0.05	0.20	10.41

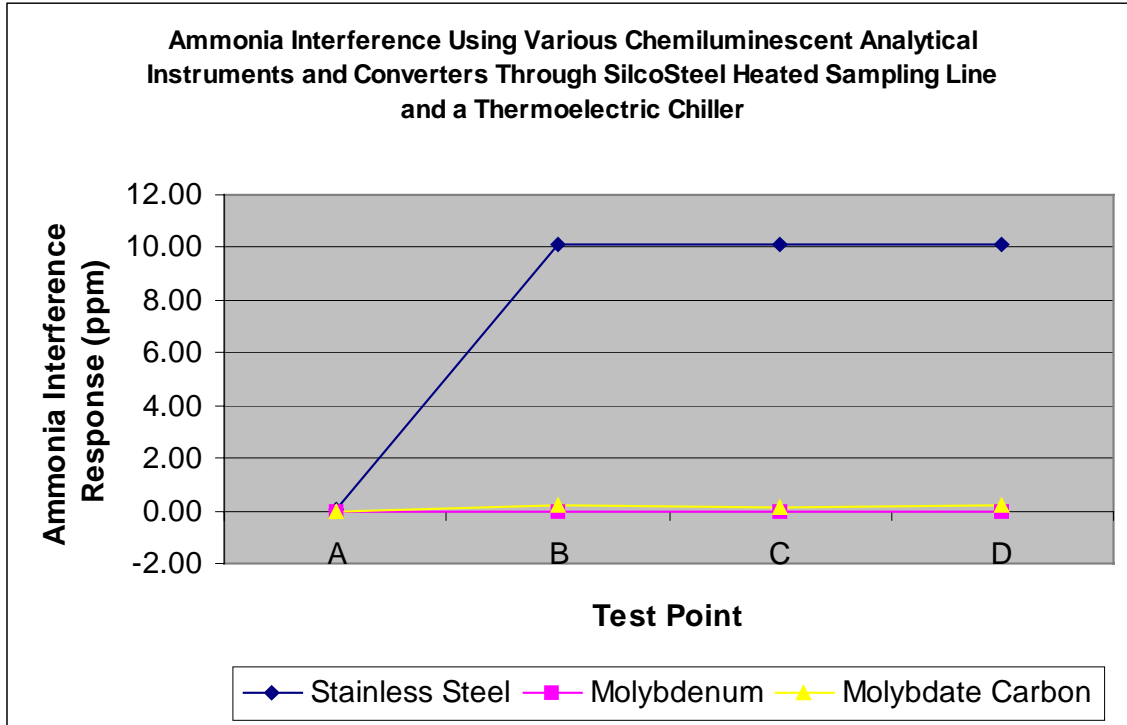


Figure 27: Silcosteel Sample Line through Thermoelectric Chiller, Ammonia and Water Only

Test 6a- Thermoelectric chiller with stainless steel sampling line

This is similar to Test 4a but with a 100 ft. stainless steel sample line instead of PFA. Figure 28 summarizes the results. Ammonia was measured with efficiencies varying from 54 to 87 percent compared with that calculated. The NO_x analyzer with the stainless steel converter was again the only one to respond to ammonia. The response of the NO_x/stainless steel converter in all cases where ammonia was input was above the analytical range (>10 ppm). The measured ammonia concentration changed very little for gas with water added as the temperature of the sampling line was increased from 25 to 175 °C. As with the PFA and Silcosteel® sample lines, we conclude that heating the sample line had no effect on ammonia penetration through the sampling line.

Test Point	Temp. (°C)	Input NH ₃ (ppmd)	Input H ₂ O % @ 191°C	SS	MOLY	MOLYC	NH ₃
				Measured NO _x (ppmd)	Measured NO _x (ppmd)	Measured NO _x (ppmd)	Measured NH ₃ (ppmd)
A	25.0	0.00	0.00	0.06	-0.05	0.01	0.02
B	25.0	14.92	0.00	10.12	-0.02	0.18	8.15
C	25.0	12.99	12.97	10.12	-0.05	0.17	11.31
D	107.0	12.99	12.97	10.12	-0.05	0.16	10.77
E	175.0	12.99	12.97	10.12	-0.05	0.19	10.36

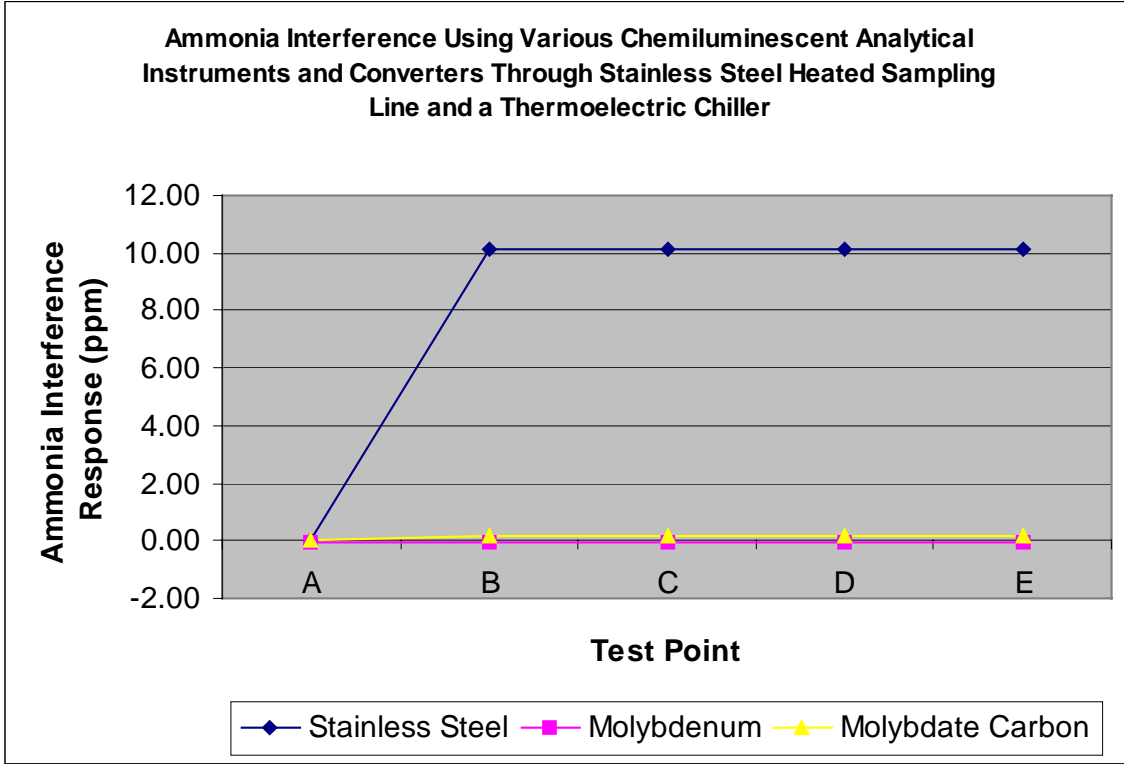


Figure 28: Stainless Steel Sample Line through Thermoelectric Chiller, Ammonia and Water Only

NH₃ and NO_x in Simulated Exhaust

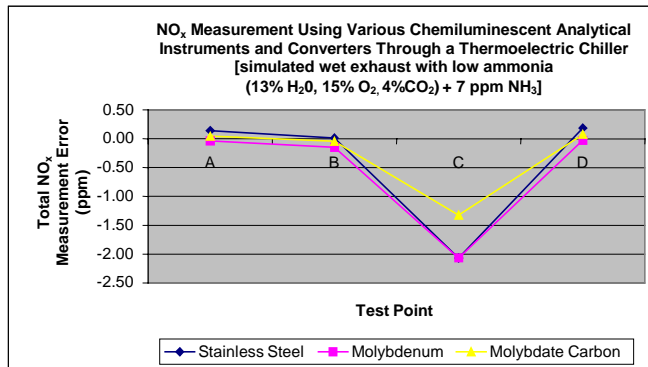
Test 1b-3b- Thermoelectric chiller (with minimal sample line length)

Figures 29, 30, and 31 summarize the results from this set of tests. The first two tests were conducted with the sample stream containing 13 percent water, with ammonia inputs of 7 ppmd and 12 ppmd, respectively. The third test was conducted with the sample stream containing 6 percent water, with and without ammonia input of 12 ppmd. Data in the figures are presented in both tabular and graphical form, with a sidebar table showing the ammonia input/measured concentrations.

The ammonia analyzer did not respond in any significant way when 7 ppm ammonia was added to the simulated exhaust. The main difference between this test and the tests conducted in the previous series was the addition of 4 percent CO₂ and the reduction in oxygen from 21 percent to 15 percent. The NO_x analyzer with the stainless steel converter also did not respond

to ammonia. The results indicate that the addition of CO₂ under these conditions results in the ammonia being adsorbed in the sampling train. The adsorption could have occurred in the thermoelectric chiller. Adding 9.7 ppm of NO_x (equal concentrations of NO and NO₂) resulted in a response from the NO_x analyzers of 77 percent-86 percent of the inputted amount. The ammonia analyzer gave a similar response to added NO_x, presumably due to the NO_x. Raising the ammonia concentration to 12 ppm resulted in a small response by the ammonia analyzer, approximately five percent of input. The ammonia analyzer response after adding NO_x (for both the 7 ppm and 12 ppm NH₃ inputs) was less than before NO_x input, indicating no memory effect. The NO_x analyzers gave similar responses to inputted NO_x, indicating that they were unaffected by the change in the ammonia concentration. Lowering the water from 13 percent to 6 percent did not change the conclusions. When ammonia was not added, the NO_x analyzer response was unaffected. There was evidence of ammonia accumulation in the stainless steel converter over time (referring to zero points from Figure 29, Figure 30, and Figure 31), although it was not as pronounced as that found in the previous set of tests.

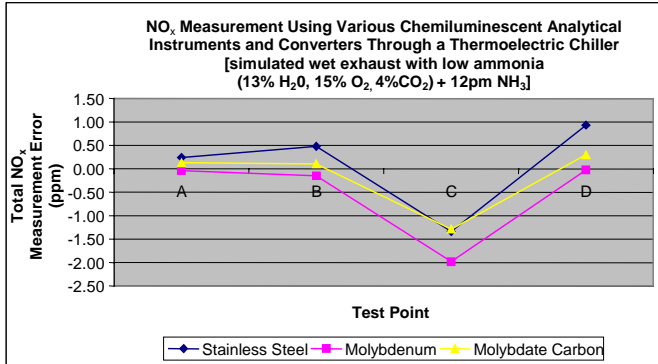
13% water, 6 ppm NH ₃ , 4% CO ₂ , 15% O ₂				SS		MOLY		MOLYC	
Test Point	Input NO (ppmd)	Input NO ₂ (ppmd)	Input NO _x (ppmd)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)
A	0.00	0.00	0.00	0.14	0.14	-0.04	-0.04	0.04	0.04
B	0.20	0.24	0.44	0.45	0.01	0.29	-0.15	0.39	-0.05
C	4.88	4.83	9.70	7.63	-2.07	7.64	-2.07	8.38	-1.33
D	0.00	0.00	0.00	0.18	0.18	-0.03	-0.03	0.07	0.07



	MOLY/MOLY C ONLY		NH ₃	
	Input NH ₃ (ppmd)	Avg Measured NO _x (ppmd)	Measured NH ₃ + NO _x (ppmd)	Measured NH ₃ (ppmd)
A	6.96	0.00	0.05	0.04
B	6.96	0.34	0.43	0.09
C	6.96	8.01	6.81	-1.20
D	6.96	0.02	0.21	0.18

Figure 29: Thermoelectric Chiller, Ammonia, Water, and NO/NO₂ Combinations

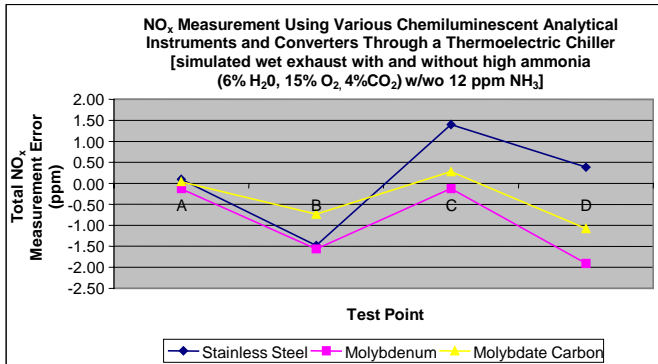
13% water, 10 ppm NH ₃ , 4% CO ₂ , 15% O ₂				SS		MOLY		MOLYC	
Test Point	Input NO (ppmd)	Input NO ₂ (ppmd)	Input NO _x (ppmd)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)
A	0.00	0.00	0.00	0.24	0.24	-0.04	-0.04	0.13	0.13
B	0.20	0.24	0.44	0.91	0.48	0.29	-0.15	0.54	0.11
C	4.88	4.83	9.70	8.36	-1.34	7.72	-1.98	8.42	-1.29
D	0.00	0.00	0.00	0.93	0.93	-0.02	-0.02	0.30	0.30



	MOLY/MOLY C ONLY		NH ₃	
	Input NH ₃ (ppmd)	Avg Measured NO _x (ppmd)	Measured NH ₃ + NO _x (ppmd)	Measured NH ₃ (ppmd)
A	11.59	0.04	0.82	0.77
B	11.59	0.41	1.24	0.82
C	11.59	8.07	7.64	-0.43
D	11.59	0.14	1.02	0.89

Figure 30: Thermoelectric Chiller, Ammonia, Water, and NO/NO₂ Combinations

6% water, 4% CO ₂ , 15% O ₂ , without/with 10 ppm NH ₃				SS		MOLY		MOLYC	
Test Point	Input NO (ppmd)	Input NO ₂ (ppmd)	Input NO _x (ppmd)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)
A	0.20	0.24	0.44	0.53	0.09	0.31	-0.13	0.48	0.04
B	4.89	4.84	9.73	8.25	-1.48	8.17	-1.56	9.00	-0.73
C	0.20	0.24	0.44	1.84	1.40	0.32	-0.12	0.72	0.28
D	4.89	4.85	9.74	10.12	0.38	7.83	-1.91	8.66	-1.08



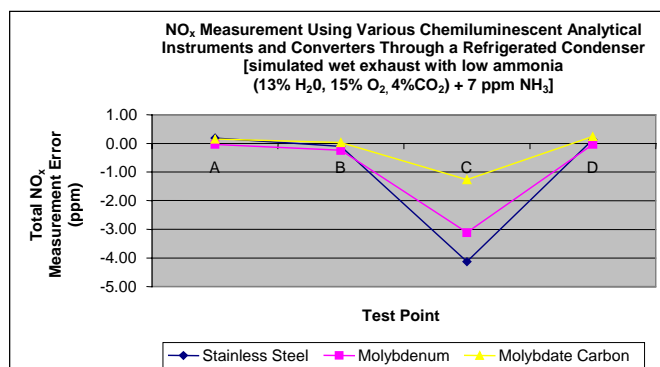
	MOLY/MOLY C ONLY		NH ₃	
	Input NH ₃ (ppmd)	Avg Measured NO _x (ppmd)	Measured NH ₃ + NO _x (ppmd)	Measured NH ₃ (ppmd)
A	0.00	0.39	0.33	-0.07
B	0.00	8.58	7.25	-1.33
C	11.63	0.52	2.92	2.41
D	11.63	8.24	10.44	2.19

Figure 31: Thermoelectric chiller, Ammonia, Water, and NO/NO₂ Combinations

Test 4b-6b- Refrigerated condenser (with minimal sample line length)

Figures 32, 33, and 34 summarize the results from these tests. Data in the figures are presented in both tabular and graphical form, with a sidebar table showing the ammonia input/measured concentrations. Adding 9.7 ppm of NO_x (equal concentrations of NO and NO₂) resulted in a response from the NO_x analyzers of 57 percent-87 percent of the inputted amount. This is similar to what was observed in tests using the refrigerated condenser. The response of the ammonia analyzer to the NO_x was again similar to that from the NO_x analyzers. Raising the ammonia concentration to 12 ppm resulted in a significant response by the ammonia analyzer (approximately 20 percent of input), indicating a greater penetration of ammonia through the refrigerated condenser than the thermoelectric chiller. The ammonia analyzer response after added NO_x was higher in this set of experiments, indicating a memory effect. This is most likely due to the presence of residual ammonia in the converter, a phenomenon that has been observed when sampling ambient air. The NO_x analyzers gave similar responses to inputted NO_x, again indicating that they were unaffected by the changes in the ammonia concentration. Lowering the water from 13 percent to 6 percent again gave results consistent with 13 percent water. There was once again evidence of ammonia accumulation in the stainless steel converter over the course of the three tests (see zero points in Figure 32, Figure 33, and Figure 34). This resulted in a positive zero bias of approximately 2 ppm by the end of the tests.

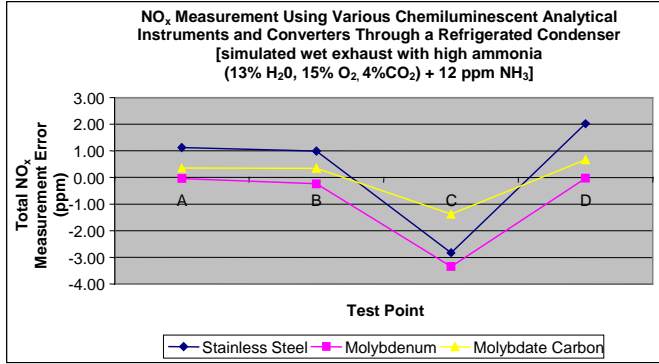
13% water, 7 ppm NH ₃ , 4% CO ₂ , 15% O ₂				SS		MOLY		MOLYC	
Test Point	Input NO (ppmd)	Input NO ₂ (ppmd)	Input NO _x (ppmd)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)
A	0.00	0.00	0.00	0.19	0.19	-0.04	-0.04	0.15	0.15
B	0.19	0.24	0.44	0.33	-0.11	0.19	-0.25	0.46	0.03
C	4.87	4.83	9.70	5.57	-4.13	6.59	-3.11	8.44	-1.27
D	0.00	0.00	0.00	0.13	0.13	-0.04	-0.04	0.23	0.23



	MOLY/MOLY C ONLY		NH ₃	
	Input NH ₃ (ppmd)	Avg Measured NO _x (ppmd)	Measured NH ₃ + NO _x (ppmd)	Measured NH ₃ (ppmd)
A	6.97	0.05	0.02	-0.03
B	6.96	0.33	0.33	0.00
C	6.96	7.51	7.27	-0.25
D	6.96	0.10	1.65	1.55

Figure 32: Refrigerated Condenser, Ammonia, Water, and NO/NO₂ Combinations

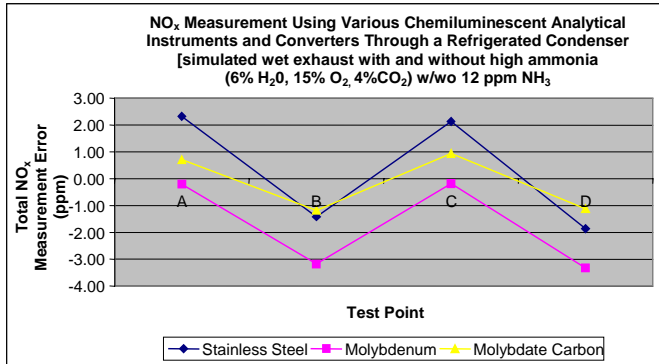
13% water, 12 ppm NH ₃ , 4% CO ₂ , 15% O ₂				SS		MOLY		MOLYC	
Test Point	Input NO (ppmd)	Input NO ₂ (ppmd)	Input NO _x (ppmd)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)
A	0.00	0.00	0.00	1.12	1.12	-0.04	-0.04	0.35	0.35
B	0.19	0.24	0.44	1.43	0.99	0.20	-0.24	0.78	0.34
C	4.88	4.83	9.71	6.88	-2.83	6.36	-3.34	8.32	-1.39
D	0.00	0.00	0.00	2.01	2.01	-0.03	-0.03	0.67	0.67



MOLY/MOLY C ONLY		NH ₃		
Input NH ₃ (ppm)	Avg Measured NO _x (ppmd)	Measured NH ₃ + NO _x (ppmd)	Measured NH ₃ (ppmd)	
A	11.59	0.16	1.21	1.05
B	11.60	0.49	3.04	2.56
C	11.60	7.34	10.36	3.02
D	11.59	0.32	2.35	2.03

Figure 33: Refrigerated Condenser, Ammonia, Water, and NO/NO₂ Combinations

6% water, 4% CO ₂ , 15% O ₂ , without/with 12 ppm NH ₃				SS		MOLY		MOLYC	
Test Point	Input NO (ppmd)	Input NO ₂ (ppmd)	Input NO _x (ppmd)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)
A	0.20	0.24	0.44	2.76	2.32	0.24	-0.20	1.15	0.71
B	4.89	4.84	9.73	8.32	-1.41	6.55	-3.18	8.55	-1.18
C	0.20	0.24	0.44	2.57	2.13	0.26	-0.18	1.38	0.94
D	4.89	4.84	9.73	7.87	-1.86	6.41	-3.33	8.62	-1.12



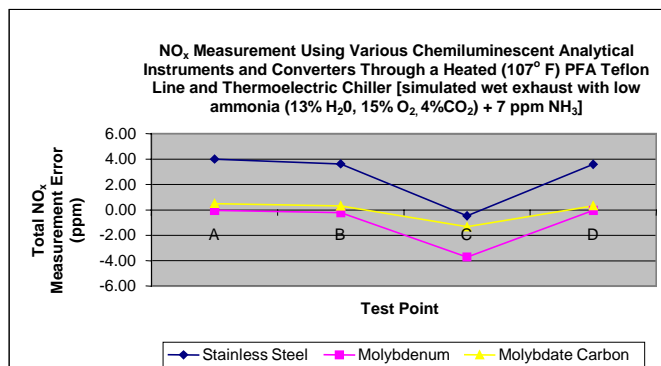
MOLY/MOLY C ONLY		NH ₃		
Input NH ₃ (ppm)	Avg Measured NO _x (ppm)	Measured NH ₃ + NO _x (ppm)	Measured NH ₃ (ppm)	
A	0.00	0.69	2.27	1.57
B	0.00	7.55	8.30	0.74
C	11.63	0.82	2.51	1.69
D	11.62	7.51	10.57	3.06

Figure 34: Refrigerated Condenser, Ammonia, Water, and NO/NO₂ Combinations.

Test 7b-9b Thermoelectric chiller with PFA sample line @ 107 °C

Figures 35, 36, and 37 summarize the results from these tests. Data in the figures are presented in both tabular and graphical form, with a sidebar table showing the ammonia input/measured concentrations. The NO_x analyzer response is at the zero point was approximately 4 ppm, leading to the conclusion that ammonia accumulation from previous tests was continuing. The response of the NO_x analyzer with the stainless steel converter to added NO_x did not rise proportionately. The NO_x response of the analyzer with the moly converter was 21 percent lower than the experiments with the sample conditioners alone, but the one with the molybdate carbon converter was the same. We conclude that the increased length of the sampling line most likely did not remove a significant amount of NO_x. Raising the ammonia to 12 ppm did not significantly change the response of any analyzer. Lowering the water from 13 percent to 6 percent again gave results consistent with 13 percent water. Not adding ammonia to the synthetic exhaust mixture system did not significantly change the response of either of the analyzers with stainless steel converters. This may be due to the slow release of ammonia in the sample line.

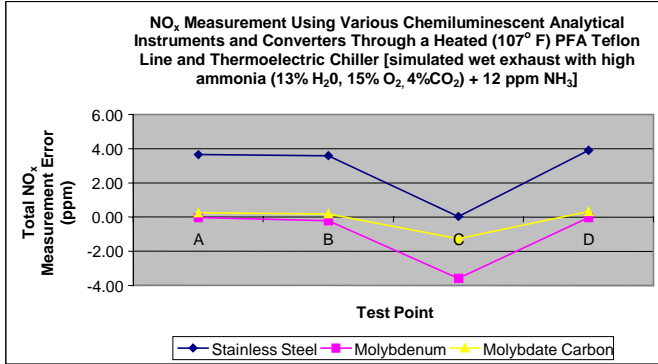
13% water, 7 ppm NH ₃ , 4% CO ₂ , 15% O ₂ PFA (107° F)				SS		MOLY		MOLYC	
Test Point	Input NO (ppmd)	Input NO ₂ (ppmd)	Input NO _x (ppmd)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)
A	0.00	0.00	0.00	3.99	3.99	-0.04	-0.04	0.49	0.49
B	0.19	0.24	0.44	4.05	3.61	0.22	-0.22	0.74	0.31
C	4.88	4.83	9.71	9.24	-0.47	5.99	-3.72	8.37	-1.34
D	0.00	0.00	0.00	3.59	3.59	-0.03	-0.03	0.31	0.31



	MOLY/MOLY C ONLY		NH ₃	
	Input NH ₃ (ppm)	Avg Measured NO _x (ppm)	Measured NH ₃ + NO _x (ppm)	Measured NH ₃ (ppm)
A	6.96	0.23	0.08	-0.14
B	6.96	0.48	0.37	-0.11
C	6.97	7.18	6.82	-0.37
D	6.96	0.14	0.10	-0.04

Figure 35: PFA Teflon Sample Line through Thermoelectric Chiller, Ammonia, Water, and NO/NO₂ Combinations

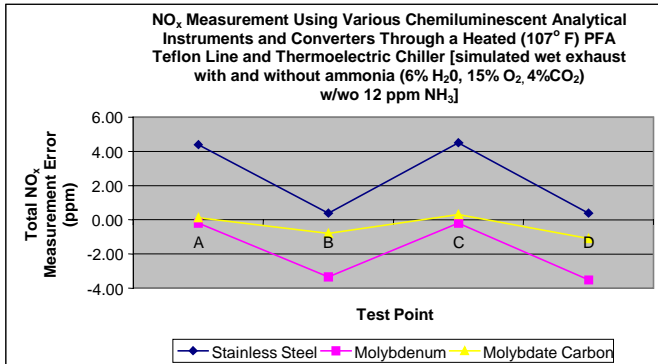
13% water, 12 ppm NH ₃ , 4% CO ₂ , 15% O ₂ PFA (107° F)				SS		MOLY		MOLYC	
Test Point	Input NO (ppmd)	Input NO ₂ (ppmd)	Input NO _x (ppmd)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)
A	0.00	0.00	0.00	3.65	3.65	-0.04	-0.04	0.25	0.25
B	0.20	0.24	0.44	4.03	3.59	0.22	-0.22	0.62	0.18
C	4.87	4.83	9.70	9.74	0.04	6.12	-3.59	8.43	-1.27
D	0.00	0.00	0.00	3.90	3.90	-0.03	-0.03	0.32	0.32



MOLY/MOLY C ONLY		NH ₃	
Input NH ₃ (ppm)	Avg Measured NO _x (ppm)	Measured NH ₃ + NO _x (ppm)	Measured NH ₃ (ppm)
A	11.60	0.11	0.42
B	11.59	0.42	0.91
C	11.59	7.28	7.45
D	11.60	0.15	0.76

Figure 36: PFA Teflon Sample Line through Thermoelectric Chiller, Ammonia, Water, and NO/NO₂ Combinations

6% water, 4% CO ₂ , 15% O ₂ , without/with PFA (107° F)				SS		MOLY		MOLYC	
Test Point	Input NO (ppmd)	Input NO ₂ (ppmd)	Input NO _x (ppmd)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)
A	0.20	0.24	0.44	4.83	4.39	0.25	-0.19	0.55	0.12
B	4.89	4.84	9.73	10.12	0.39	6.40	-3.34	8.93	-0.80
C	0.20	0.24	0.44	4.94	4.50	0.25	-0.19	0.75	0.31
D	4.89	4.84	9.73	10.12	0.39	6.22	-3.51	8.64	-1.09



MOLY/MOLY C ONLY		NH ₃	
Input NH ₃ (ppm)	Avg Measured NO _x (ppm)	Measured NH ₃ + NO _x (ppm)	Measured NH ₃ (ppm)
A	0.00	0.40	0.34
B	0.00	7.66	7.22
C	11.63	0.50	2.93
D	11.63	7.43	10.07

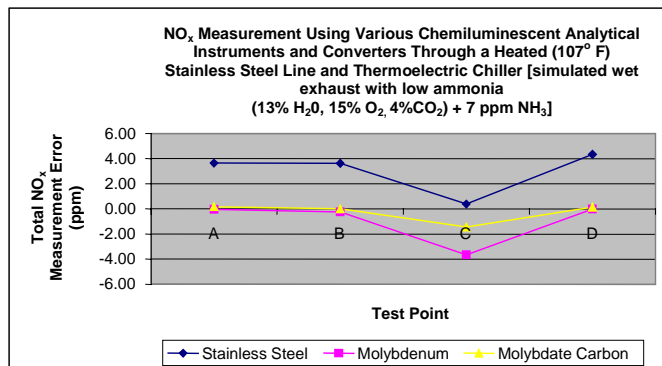
Figure 37: PFA Teflon Sample Line through Thermoelectric Chiller, Ammonia, Water, and NO/NO₂ Combinations

Test 10B-12b- Thermoelectric chiller with stainless steel sample line @ 107 °C

Figures 38, 39, and 40 summarize the results from these tests. Data in the figures are presented in both tabular and graphical form, with a sidebar table showing the ammonia input/measured concentrations. The highlight from both of these sampling lines was the significant response from the NO_x analyzer with stainless steel converters whether ammonia was present or not, indicating ammonia accumulation.

Figure 41 graphically presents this explanation, showing the zero NO_x input points for the entire set of tests. As shown in the graph, there was significant and increasing positive bias in the NO_x analyzer with the stainless steel converter beginning during the tests of the refrigerated condenser and continuing through the tests of the sample lines. This phenomenon was also observed in plots of the low NO_x input (0.44 ppm) and high NO_x input (9.7 ppm). The phenomenon was not observed in any of the other analyzers, including the ammonia analyzer (which uses a high temperature stainless steel converter). It is concluded from these observations that there is significant ammonia hang-up in the stainless steel converter operated at 350°C.

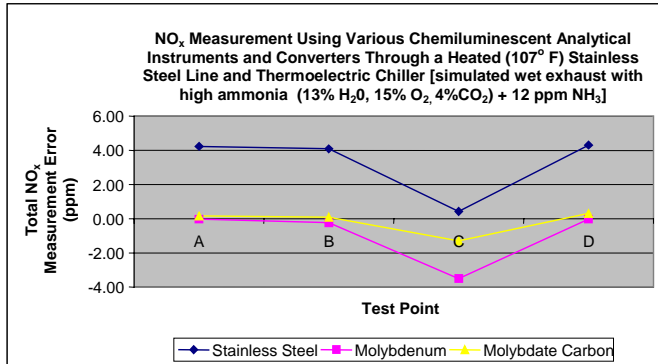
13% water, 7 ppm NH ₃ , 4% CO ₂ , 15% O ₂ SS (107° F)				SS		MOLY		MOLYC	
Test Point	Input NO (ppmd)	Input NO ₂ (ppmd)	Input NO _x (ppmd)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)
A	0.00	0.00	0.00	3.64	3.64	-0.03	-0.03	0.17	0.17
B	0.19	0.24	0.44	4.06	3.63	0.20	-0.24	0.44	0.00
C	4.88	4.83	9.71	10.09	0.39	6.06	-3.65	8.27	-1.44
D	0.00	0.00	0.00	4.35	4.35	-0.02	-0.02	0.15	0.15



MOLY/MOLY C		NH ₃	
Input NH ₃ (ppmd)	Avg Measured NO _x (ppmd)	Measured NH ₃ + NO _x (ppmd)	Measured NH ₃ (ppm)
6.97	0.07	0.07	-0.01
6.96	0.32	0.38	0.07
6.96	7.17	6.67	-0.50
6.96	0.06	0.18	0.12

Figure 38: Stainless Steel Sample Line through Thermoelectric Chiller, Ammonia, Water, and NO/NO₂ Combinations

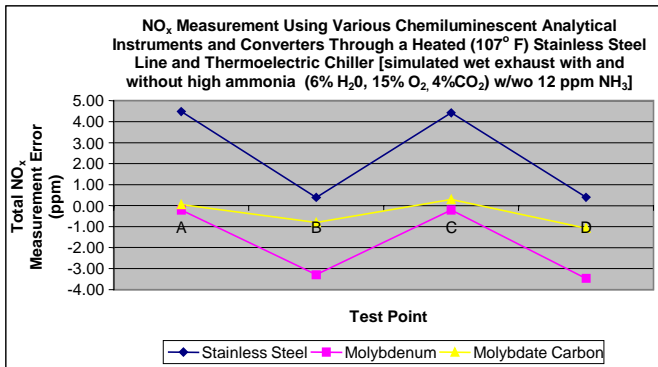
13% water, 12 ppm NH ₃ , 4% CO ₂ , 15% O ₂ SS (107° F)				SS		MOLY		MOLYC	
Test Point	Input NO (ppmd)	Input NO (ppmd)	Input NO _x (ppmd)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)
A	0.00	0.00	0.00	4.22	4.22	-0.03	-0.03	0.16	0.16
B	0.20	0.24	0.44	4.53	4.09	0.21	-0.23	0.53	0.09
C	4.87	4.83	9.70	10.12	0.42	6.19	-3.51	8.40	-1.30
D	0.00	0.00	0.00	4.31	4.31	-0.02	-0.02	0.31	0.31



MOLY/MOLY C ONLY		NH ₃	
Input NH ₃ (ppmd)	Avg Measured NO _x (ppmd)	Measured NH ₃ + NO _x (ppmd)	Measured NH ₃ (ppm)
11.59	0.07	0.67	0.60
11.59	0.37	1.13	0.77
11.59	7.29	7.46	0.16
11.59	0.14	0.93	0.78

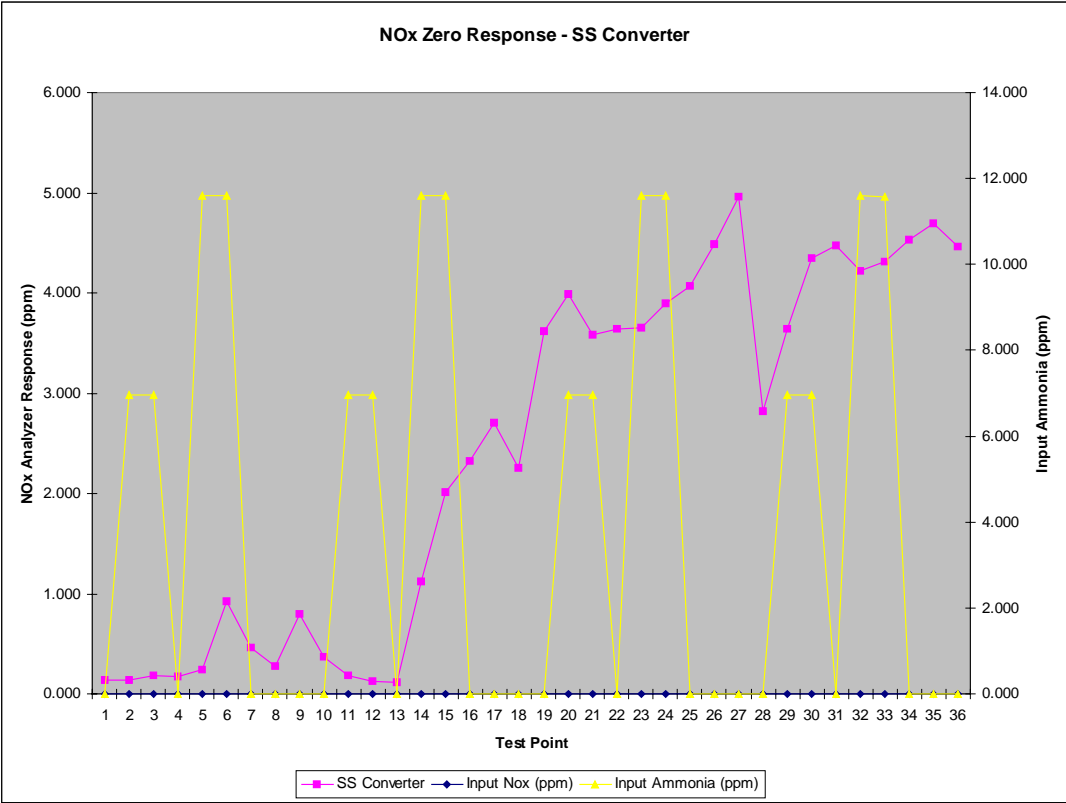
Figure 39: Stainless Steel Sample Line through Thermoelectric Chiller, Ammonia, Water, and NO/NO₂ Combinations

6% water, 4% CO ₂ , 15% O ₂ , without/with SS (107° F) 12 ppm NH _x				SS		MOLY		MOLYC	
Test Point	Input NO (ppmd)	Input NO ₂ (ppmd)	Input NO _x (ppmd)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)	Measured NO _x (ppmd)	difference (ppm)
A	0.20	0.24	0.44	4.92	4.48	0.23	-0.21	0.49	0.05
B	4.89	4.84	9.73	10.12	0.39	6.44	-3.30	8.93	-0.80
C	0.20	0.24	0.44	4.85	4.41	0.23	-0.20	0.74	0.30
D	4.89	4.84	9.73	10.12	0.39	6.26	-3.46	8.65	-1.08



MOLY/MOLY C ONLY		NH ₃	
Input NH ₃ (ppmd)	Avg Measured NO _x (ppmd)	Measured NH ₃ + NO _x (ppmd)	Measured NH ₃ (ppm)
0.00	0.36	0.30	-0.06
0.00	7.68	7.15	-0.53
11.63	0.49	3.19	2.70
11.62	7.46	10.14	2.68

Figure 40: Stainless Steel Sample Line through Thermoelectric Chiller, Ammonia, Water, and NO/NO₂ Combinations



Test Points	Equipment Tested
1-9	Thermoelectric chiller
10-18	Refrigerated condenser
19-27	PFA sample line
28-36	Stainless steel sample line

Figure 41: Chronological NO_x Analyzer (with Stainless Steel Converter) Response at Zero NO_x Input Points

5.0 Conclusions and Recommendations

5.1 Analyzer Performance Testing

Five types of chemiluminescent NO_x analyzers were evaluated during the course of the test program. For the dilution extractive analysis, a TECO Model 42CY chemiluminescence analyzer with a range of 1 ppb to 1.0 ppm and a molybdate carbon converter was utilized. For all other analyses, TECO Models 42 and 10 chemiluminescence analyzers with full-scale ranges of 0-10 ppm were utilized. Three “dry” chemiluminescence analyzers with different NO₂ to NO converters (stainless steel, molybdenum, and molybdate carbon) were evaluated simultaneously through all phases of the test program. Two other chemiluminescent analyzers were evaluated concurrently with the other instruments; one that was designed with a vitreous carbon converter placed upstream of the sample conditioning system, and another designed to measure “hot/wet” sample streams using an upstream molybdate carbon converter.

NO₂ to NO converter efficiencies ranged from 83 percent to 97 percent. Only the two hot/wet converters had efficiencies less than 90 percent (83 percent and 86 percent for the vitreous carbon and hot/wet molybdate carbon converters, respectively). Converter efficiencies greater than 90 percent are considered acceptable. As converter efficiency is highly dependent on history, we were unable to determine the reasons behind the low converter efficiencies for these instruments. These two converters, however, were used in the alternative sampling systems, and therefore were not necessary for the evaluation of the sample conditioning systems and sample lines.

Analyzer linearity response for all analyzers was excellent except for the source level analyzer using the standard molybdate carbon converter. Linearity for this instrument was 2.2 percent, greater than the acceptable limit of two percent.

The only interferent gas that led to a response in any of the analyzers was ammonia, which created a positive response in all converter/analyzer combinations except for the instrument using the vitreous carbon converter. The interference bias was highest for the NO_x analyzer with the stainless steel converter, as would be expected. There was a significant response from the analyzer using the molybdate carbon converter (~10 percent), and a slight response from the analyzer with the molybdenum converter (~3 percent).

Analyzer drifts were all less than 1 percent over the course of the 14-hour drift test, except for the analyzer with the hot/wet molybdate carbon converter. This instrument exhibited drifts of five percent, seven percent, and six percent at the 6 hr., 10 hr., and 14 hr. evaluation points.

5.2 Sample Conditioning Systems

Five types of sample conditioners were evaluated in this test program: a permeation dryer, a combination ambient condenser/permeation dryer, a thermoelectric chiller, a refrigerated coil-type condenser, and a Method 5-style sampling train with impingers in an ice bath. A sixth type (dilution extractive probe) is discussed in Section 5.2.

The most significant finding was that no ammonia was detected at the analyzer sampling manifold throughout testing of all sample conditioners, except for a slight amount (<1 ppm)

detected at a few conditions while testing the refrigerated condenser and impingers in an ice bath. This phenomenon is discussed at length in Section 5.2.

In general, use of the sample conditioning systems resulted in measured NO_x values that were lower than input values, except for a few test conditions using the refrigerated condenser and impingers in an ice bath (resulting in a slight positive bias). The greatest differences (approximately -10 percent to -25 percent of input concentration) occurred at the lowest NO_x input conditions (0.2/0.2 ppm NO/NO₂). Losses measured at all other conditions (>2ppm input NO_x) were all less than 10 percent. The larger differences in the first case are most likely due to analyzer error, as all instruments were operating on a 0-10 ppm analytical range. The input concentrations, therefore, were approximately 4 percent of the analytical range. Most continuous monitoring protocols specify that the sample concentration fall between 20 percent and 95 percent of the analyzer operating range. We recommend that future low-NO_x evaluation should include instruments with a low enough analytical range to meet this criteria. Of the sample conditioning systems tested, the permeation dryer and thermoelectric chiller resulted in the greatest differences.

It is interesting to note that no differences were observed with any sample conditioning system due to water input. Test conditions using 6 percent water and 13 percent water input were statistically no different from dry simulated exhaust with respect to NO_x measurement. We conclude that each of the conditioners tested performed well as far as moisture removal and/or minimizing contact of the sample gas with condensed water. Of further interest is that the results show approximately 30 percent increased loss (relative to baseline wet exhaust case) for all conditioning systems tested when ammonia is added to the wet sample stream. This is discussed further in Section 5.3.

5.3 Sample Lines

Three types of sample lines were evaluated in this test program: PFA Teflon, 316L stainless steel, and 316L Silcosteel® (stainless steel with a thin glass lining). The lines were evaluated at three temperatures (25 °C, 107 °C, and 175 °C). All sample lines were evaluated with the three chemiluminescent analyzers downstream of the same reference sample conditioner (the thermoelectric chiller).

In combination with the reference sample conditioner, average losses through the sample lines were approximately 20 percent for the low NO_x (0.2 ppm NO, 0.2 ppm NO₂) conditions, 5 percent for the conditions with 1 ppm/1 ppm and 4.7 ppm/4.7 ppm NO/NO₂ inputs, and 2 percent for the 9 ppm/1 ppm NO/NO₂ conditions. Average losses through the thermoelectric chiller alone for the same three sets of conditions (from the previous tests) were 23 percent, 10 percent, and 7 percent, respectively. As a result, we conclude that the majority of NO_x losses in measurement systems occur in the sample conditioning systems, and not the sample lines.

There were no statistical differences observed between any of the sample line test conditions, regardless of material used or operating temperature. The only exception was that, in the presence of ammonia and water, NO_x losses increased (for the lowest NO_x input) in the stainless steel line operating at 175 °C. This was not observed in the stainless steel line operating at 25 °C for the same conditions. We conclude that, under these conditions, there are interactions between NO and/or NO₂ with ammonia that occur at elevated temperatures,

leading to NO_x losses in the stainless steel sampling line. Further study is recommended to determine the exact nature of these interactions.

5.4 Alternative Sampling Systems

Three types of alternative sampling systems were evaluated in this test program: a system with an up-front NO₂ to NO converter followed by a thermoelectric chiller, a hot/wet molybdate carbon converter and analyzer with no moisture knockout, and a dilution extractive system using a molybdate carbon converter.

Overall, the measured differences relative to the input NO_x concentrations for these three systems (2 percent to 35 percent) was higher than those observed in the traditional sampling systems (2 percent to 20 percent) under the tested conditions. Furthermore, these differences changed more dramatically than the traditional systems with changing conditions, in some cases shifting results from a high positive bias to a high negative bias with a slight change in input gas composition.

For the analyzer with the hot/wet vitreous carbon converter, results show an increasing negative bias as a function of NO₂ input concentration (from ~20 percent at 0.2 ppm NO₂ input to ~30 percent at 4.7 ppm NO₂ input). This is most notable at test conditions with ammonia present. It is suspected that there is a chemical and/or physical interaction of NO₂ with ammonia in the vitreous carbon converter. This could be related to, in part, the low converter efficiency measured at the start of the test program. Further study is recommended to determine the exact nature of these interactions.

For the analyzer with the hot/wet molybdate carbon converter, results show that the addition of water to the sample stream resulted in a positive bias in all cases, and increased as a function of water input (~3 percent average bias for dry simulated exhaust, ~7 percent average bias for wet [6 percent H₂O] simulated exhaust, and ~19 percent bias for wet [13 percent H₂O] simulated exhaust). The addition of ammonia to the sample stream resulted in a negative effect on NO_x readings at low concentrations, but a positive effect on NO_x readings at higher concentrations. In general, the percentage absolute error increased with increasing NO_x concentrations. It is obvious from the results that there are interactions between ammonia, NO_x, and water in the molybdate carbon converter. These interactions are most likely related to those observed in the previous cases, and warrant further study to provide recommendations to reduce their impacts on measurement of low NO_x concentrations.

For the analyzer using the dilution extraction probe, there was a consistent negative bias on measured versus input NO_x concentrations. This could be a result of dilution error, possibly from an incorrect calibration of the dilution airflow control and/or sample flow control systems. Results indicate in increasing absolute bias (negative) with increasing NO₂ concentrations. It is unclear whether this effect is due to the dilution extraction probe itself or the molybdate carbon converter used with the ambient level analyzer. Based on results from the analyzer with the hot/wet molybdate carbon converter, it would suggest that this bias occurs due to interactions in the converter.

5.4.1 Additional Ammonia Effects Evaluation

As a follow-up to the unusual results observed during the initial testing of sample conditioning systems and sample lines, additional testing was performed to more conclusively determine the effects of potential ammonia concentrations in combustion sources with low concentrations of NO_x. Once again, synthetically-prepared mixtures of pure gases and simulated exhaust gases were generated and passed through various sample lines and sample conditioning systems into the chemiluminescent analyzers with various NO₂ to NO converters.

When CO₂ was not present in the sample stream (wet or dry), most of the ammonia (74 percent to 88 percent) penetrated through the refrigerated condenser and thermoelectric chiller sample conditioning systems tested, both with and without water. Less ammonia (53 percent to 59 percent) penetrated through the glass impingers in an ice bath, but it still represented a majority of the input concentrations, in contrast to observations of no ammonia penetration in previous tests where CO₂ and water were both present.

Only the NO_x analyzer with the stainless steel converter responded significantly to ammonia. The ammonia response from the stainless steel converter increased with increasing water input.

There was evidence of ammonia hang-up in the NO_x/stainless steel converter and ammonia sampling systems after the ammonia input was shut off. This effect was more pronounced in the NO_x/stainless converter than the ammonia/high temperature stainless converter, suggesting that the hang-up occurs in the converter itself, rather than in the sample conditioning systems.

The response of the NO_x analyzer with the stainless converter to ammonia was similar for all three types of water removal systems (refrigerated condenser, impingers in an ice bath, thermoelectric chiller).

The sample line material and operating temperature had no effect on ammonia penetration. The reason may be that the ammonia vapor was in equilibrium with the liquid water (at the ambient 25 °C condition) that undoubtedly condensed in the sampling line. The ammonia losses in the sample lines (for all materials and temperatures tested) were minimal. A comparison of results between the various sample line/thermoelectric chiller tests and those using the thermoelectric chiller alone showed that the majority of the small overall ammonia loss occurred in the sample conditioner.

Adding CO₂ to the synthetic exhaust appears to result in the removal of ammonia in the sampling train upstream of the sampling points of the NO_x and NH₃ analyzers. This may be the result of acidification of water in the sample stream from CO₂.

It is suspected that ammonia accumulates in the low temperature (NO_x) stainless steel converter over time, causing an increasing positive bias. This effect is more pronounced when using the refrigerated condenser for moisture removal. Overall, the results obtained were similar whether a refrigerated condenser or thermoelectric chiller was used to remove water.

The addition of a various sampling lines had very little effect on NO_x measurements compared with results using the sample conditioners only. Once again, there appeared to be an ammonia

accumulation phenomenon in the NO_x analyzer stainless steel converter during the sample line testing. Similar results were obtained for both PFA and stainless steel sampling lines.

Although there were some inconsistencies in the data, several significant conclusions were drawn from these experiments: Without added CO₂, ammonia was detected in similar concentrations to those input through all sample line materials/temperatures, and sample conditioning systems. Neither the sample line material/temperature nor choice of sample conditioner had a significant effect on the ammonia detected when CO₂ was not present. The exception was the glass impingers in an ice bath, which removed more ammonia than the other systems. Even in this case, however, the majority of ammonia penetrated through to the converters.

When CO₂ was included, virtually no ammonia could be measured. Some ammonia was detected at the 6 percent water input case, but very little of the input in all test cases was detected when CO₂ and water were both present.

There was an ammonia accumulation effect observed in the stainless steel NO_x converter. Results suggest that ammonia is accumulated and subsequently converted to NO over a relatively long period of time (>1 hr). This phenomenon was not observed in any other converter, including the high temperature stainless steel converter associated with the ammonia analyzer. The effect was also not present in the stainless steel heated sampling line, perhaps due to its relatively new (unoxidized) condition.

When using synthetic exhaust, neither the sample line material/temperature affected the ammonia nor NO_x measured. Both PFA and stainless steel sampling lines at 107°C behaved in a similar manner for both ammonia and NO_x penetration.

In all cases, the molybdenum-based converter showed no response to ammonia.

The inconsistencies in the data are likely due to conditioning times required for sample line components and the converters used in the analyzers. We have found similar conditioning effects when using chemiluminescent analyzers to measure nitrogenous species in ambient air. In these cases, the converters' efficiency and memory effect for ammonia and nitric acid appear to depend on the concentrations of these species, and the prior sampling concentrations. Similar conditioning may be occurring in these experiments with synthetic exhaust. The results show that long-term sampling (>2 hours) for each condition may be required to obtain consistent readings. Due to the limited schedule and funding for the current program, we were not able to fully evaluate this effect.

5.5 Benefits to California

Accurate and precise measurements of NO_x emissions from new and near-term power generation processes are critical for determining compliance as well as offsets for NO_x credit trading programs. Many new plants use SCR for NO_x control. Efficient and cost-effective plant operation (through feedback control) requires NO_x monitoring at inlet to the SCR, and NO_x/NH₃ monitoring at the outlet of the SCR. These monitors, therefore, must be accurate, precise, and durable. The ability to quantify sources of error in NO_x measurement methods in application to low-NO_x and new-technology emission sources directly benefits the rate payer of

California by allowing the accuracy and precision necessary to determine compliance with clean air statutes and requirements.

5.6 Recommendations

As the advancement of combustion and after treatment technologies occur, we are challenged by our ability to measure increasingly lower levels of NO_x emissions. In many cases, this involves measurement of emissions in source exhausts with pollutant concentrations comparable to ambient levels. Further complicating the issue are by-products from control technologies themselves; specifically, ammonia used in control systems to eliminate NO_x emissions. A great deal of work remains to develop and implement measurement systems that can meet this challenge. The following recommendations represent responses to some of the issues that need to be addressed as we face these challenges in the years to come.

We recommend that future low-NO_x evaluation should include instruments with low enough analytical ranges to meet protocol requirements of sample concentrations of at least 20 percent of sample range. We conclude that, under these conditions, there are interactions between NO and/or NO₂ with ammonia that occur at elevated temperatures, leading to NO_x losses in the stainless steel sampling line. Further study is recommended to determine the exact nature of these interactions.

It is suspected that there is a chemical and/or physical interaction of NO₂ with ammonia in the vitreous carbon converter. It is obvious from the results that there are interactions between ammonia, NO_x, and water in the molybdate carbon converter. These interactions are most likely related to those observed in the previous cases, and warrant further study to provide recommendations to reduce their impacts on measurement of low NO_x concentrations. Based on results from the analyzer with the hot/wet molybdate carbon converter, it would suggest that biases occur due to interactions in the converter. Results show that long-term sampling (>2 hours) for each condition may be required to obtain consistent readings. Due to the limited schedule and funding for the current program, we were not able to fully evaluate this effect. A future study would allow for long-period sampling that would reveal the exact nature of ammonia accumulation and NO_x measurement effects.

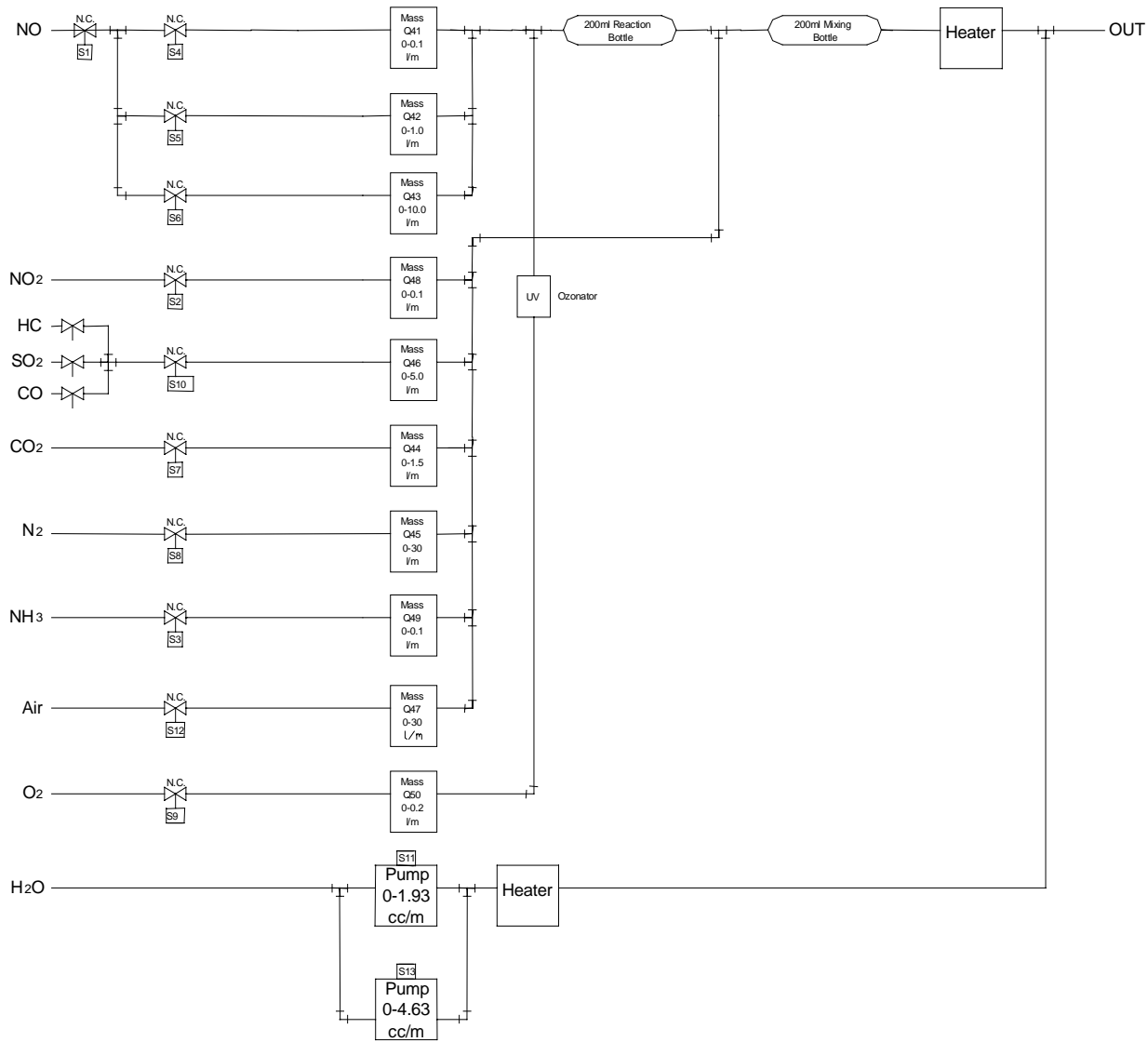
Further study is also recommended to evaluate ammonia losses in sample streams in the presence of CO₂. A potential test matrix would include simulated sample streams with multiple CO₂ and ammonia concentrations. Each test point would be evaluated with and without water vapor present.

6.0 References

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Appendix I

Dilution Calibrator and Gas Blending System



Appendix II

Detailed Test Matrix

NO_x Measurement System Detailed Test Matrix

Test 0 – Gas Evaluation

Verification that house nitrogen and cylinder zero air have no response (positive or negative) on NO_x-box.

Calibration of TE 42 NO_y using the scrubbed ambient air system (0-200 ppb range). Switched to house nitrogen and look at this “zero.” Switched to cylinder zero air and observe this “zero.”

Test 1 – Calibration (Section 3.1.1)

Nitrogen zero, 40%, 80% span checks – all ranges used

(Gas divider and 10 ppm cylinder)

Three TE 42 NO_x's and one CAI 400 HCLD operating on 0-10 ppm range.

One TE 42 NO_x with an ammonia converter operating on the 0-10 ppm range.

Input (NO/NO₂): 0/0, 4/0, 8/0

The TE 42CY NO_y operating on the 0-200 ppb range is used too low a range to use direct injection.

Test 2 - Calibration curve (Section 3.1.3)

11-point (0 to 100%) calibration, **repeated 3 times.**

Used mass Q system

Three TE 42 NO_x's and one CAI 400 HCLD operating on 0-10 ppm range.

One TE 42 NO_x with an ammonia converter operating on the 0-10 ppm range.

Input dry NO concentrations of 10-, 9-, 8-, 7-, 6-, 5-, 4-, 3-, 2-, 1-ppm, and 0.

One TE 42CY NO_y operating on the 0-200 ppb range.

Input dry NO concentrations of 200-, 180-, 160-, 140-, 120-, 100-, 80-, 60-, 40-, 20-ppb, and 0.

The heated Horiba converter followed by sample conditioner calibrated here. An additional 0-10 ppm NO_x-box was added for the three replicate calibrations.

Test 3 – Converter efficiency (Section 3.1.2)

GPT at 60%, 30% and 10% of all ranges used

Input 9-ppm into the 5 units operating on the 0-10 ppm range

Ozone turned on and set to obtain NO₂ of 6-, 3-, and 1-ppm. Measured these with 5 NO_x-boxes as well as with TDLAS and NO₂/PAN GC.

Input 180-ppb into the TE NO_y operating on the 0-200 ppb range.

Ozone turned on and set to obtain NO₂ of 120-, 60- and 20-ppb. Measured this with NO_x-box as well as with TDLAS and NO₂/PAN GC.

Note: the heated converter followed by chiller included here.

Test 3B – NO₂ calibration with cylinder gas

It was more convenient to blend cylinder NO and NO₂ instead of using NO cylinder gas and GPT for the subsequent tests. Hence, this test was added to verify the NO₂ cylinder gas.

Input NO/NO₂: 9/0, 3/6, 6/3, and 8/1-ppm into the 5 units operating on the 0-10 ppm range. Measured these with 5 NO_x-boxes as well as with TDLAS and NO₂/PAN GC.

Input NO/NO₂: 180/0, 60/120, 120/60, and 160/20-ppb into the TE NO_y operating on the 0-200 ppb range. Measure this with NO_x-box as well as with TDLAS and NO₂/PAN GC.

Note: the heated converter followed by chiller was included here.

Test 4 – Cross sensitivity (Section 3.1.4)

N₂, Air, 100 ppm CO, 15% CO₂, 500/100/60 HC, 6 & 10 ppm NH₃, 10 ppm SO₂
Added 4% CO₂ to the test. Checked these at NO/NO₂ concentrations of:

0/0, 0.2/0.2, 1/1, and 4/5 ppm

Note: the TE 42 NO_y on the 0-200 ppb scale, the TDLAS and the NO₂/PAN GC was connected to the 50:1 dilution probe for these tests.

Added sensitivity to 6% and 13% H₂O for instruments on the 50:1 dilution line and the unit with the NO₂ converter and chiller in line as part of its “normal” operation.

Input the following NO/NO₂ z/s points using N₂ as the diluent: 0/0, 0.2/0.2, 1/1, 4/5 and 0/0 ppm.

Input the following NO/NO₂ z/s points using zero air as the diluent: 0/0, 0.2/0.2, 1/1, 4/5 and 0/0 ppm.

Input the following NO/NO₂ z/s points using .85N₂/.15O₂ as the diluent: 0/0, 0.2/0.2, 1/1, 4/5 and 0/0 ppm.

Using the 85/15 N₂/O₂ diluent, input 100 ppm CO and do NO/NO₂ z/s points: 0/0, 0.2/0.2, 1/1, 4/5 and 0/0 ppm.

Using 85/15 N₂/O₂ diluent, input 15% CO₂ and do NO/NO₂ z/s points: 0/0, 0.2/0.2, 1/1, 4/5 and 0/0 ppm.

Using 85/15 N₂/O₂ diluent, input 4% CO₂ and do NO/NO₂ z/s points: 0/0, 0.2/0.2, 1/1, 4/5 and 0/0 ppm.

Using 85/15 N₂/O₂ diluent, input the HC mix and do NO/NO₂ z/s points: 0/0, 0.2/0.2, 1/1, 4/5 and 0/0 ppm.

Using 85/15 N₂/O₂ diluent, input 6 ppm NH₃ and do NO/NO₂ z/s points: 0/0, 0.2/0.2, 1/1, 4/5 and 0/0 ppm.

Using 85/15 N₂/O₂ diluent, input 10 ppm NH₃ and do NO/NO₂ z/s points: 0/0, 0.2/0.2, 1/1, 4/5 and 0/0 ppm.

Using 85/15 N₂/O₂ diluent, input 10 ppm SO₂ and do NO/NO₂ z/s points: 0/0, 0.2/0.2, 1/1, 4/5 and 0/0 ppm.

For instruments on dilution probe and the unit with upstream converter followed by chiller only:

Using 85/15 N₂/O₂ diluent, input 13% H₂O and do NO/NO₂ z/s points: 0/0, 0.2/0.2, 1/1, 4/5 and 0/0 ppm.

Using 85/15 N₂/O₂ diluent, input 6% H₂O and do NO/NO₂ z/s points: 0/0, 0.2/0.2, 1/1, 4/5 and 0/0 ppm.

Test 5 - Instrument Drift (Section 3.1.5)

2, 4, and 6 hour Z/S drift checks

Did hourly Z/S checks overnight throughout study. At a minimum, 15 minutes of N2-Zero followed by 15 minutes of 80% span on one range, went to ambient for 30 minutes, then repeat.

Placed a three way solenoid in circuit to TE 42CY NO_y on the 0-200 ppb range so that it was only inline for the zero and 160 ppb spans:

Input each of the following NO concentrations for 15-minutes: 0-ppb, 160-ppb, 8-ppm, ambient air.

Repeated the above sequence for twelve hours.

Test 6 – Sample Conditioning Systems (Section 4.1)

Sample conditioning systems were tested with dry and wet NO/NO₂ gas with CO₂, with and without the potential interferent: NH₃ (at 6-and 10-ppm)

Test 6a – dilution extraction probe

Test 6b – upstream NO₂ converter followed by thermoelectric chiller then NO_x-box

Test 6c – HCLD

Test 6d – Permeation Dryer (with ammonia removal)

Test 6e – thermoelectric chiller with glass impingers

Test 6f – refrigerated (coil-type) condenser

Test 6g – glass impinger train submerged in an ice bath

Test 6h - dual technique (ambient temperature removal followed by a permeation dryer)

Note: test 6a, test 6b, and test 6c, were performed/included with tests 6d-6h. The TE 42CY NO_y, TDLAS and NO₂/PAN GC all measured from the dilution extraction probe for all tests.

The CAI HCLD sampled directly from the hot, high dew point sample.

The Horiba NO₂ converter/chiller/NO_x-box also sampled directly from the hot, high dew point sample

The three TE 42 NO_x's with the three different types of converters and the TE 42 NO_x with the NH₃ converter all measured the effluent from the device being tested in Tests 6d-6h.

Hence a total of five tests were performed as follows:

Inputs (NO/NO₂):

- | | calib. point | |
|---|--------------|------------------------|
| • Without water: | | 0/0, 0.2/0.2, 1/1, |
| 5/5, 9/1, 0/0 | 1-6 | |
| • With 13% water: | | 0/0, 0.2/0.2, 1/1, |
| 5/5, 9/1, 0/0 | 7-12 | |
| • With 13% water, NH ₃ =6 ppm: | | 0/0, 0.2/0.2, 5/5, 0/0 |
| 13-16 | | |
| • With 13% water: | | 0/0 |
| 17 | | |

- With 13% water, NH₃=10 ppm: 0/0, 0.2/0.2, 5/5, 0/0
18-21
- With 13% water: 0/0
22
- With 6% water: 0/0, 0.2/0.2, 5/5
23-25
- With 6% water, NH₃=10 ppm: 0.2/0.2, 5/5
26-27
- With 6% water: 0/0
28
- Without water: 0/0, 5/5, 9/1, 0/0
29-32

Test 7 – Heated Sample Lines (Section 4.2)

Sample lines were tested with dry and wet NO/NO₂ gas with CO₂, with and without the potential interferent: NH₃ (at 6-and 10-ppm). The thermoelectric chiller was placed inline with all tested heated lines.

Two heated lines were tested simultaneously: the “dry” instruments (those downstream of the chiller) sampled from one heated line while the HCLD and Horiba converter/chiller/NO_x-box sampled from a second heated line.

Simultaneously, the TE 42CY NO_y, TDLAS and NO₂/PAN GC all measured from the dilution extraction probe – which sampled at the same point as the heated lines. A 100 ft long length of PFA Teflon tubing was placed between these analyzers and the dilution extraction probes for this test series to identify any losses associated with use of a long sample line with this probe.

Test 7a – 100 feet long PFA-Teflon heated line (3/8” OD)

Test 7b – 100 feet long 316L SS heated line (3/8” OD)

Test 7c – 100 feet long 316L Silcosteel[®] coated heated line (3/8” OD)

These lines were tested at temperatures of ambient (25°C), 107°C (225°F), and 175°C (350°F).

The 100 feet long lines were all contained in the same heated bundle. Hence, it was more convenient to perform test on all lines at one temperature, then move to the next temperature.

Note: the ambient temperature testing was performed with the 51°C dew point sample. (This “water mess” test was being performed to assess if viable data could be obtained should there be a failure in the sample line heating system.)

The gas inputs show for the Test 6’s were input for Tests 7a-7d for the 25°C, 107°C and 175°C tests.

Appendix III

Summary Audit Report

SUMMARY OF AUDIT RESULTS

On March 14, 2001 a quality assurance performance audit was conducted on selected NO/NO_x analyzers assembled for experiments performed for the California Energy Commission (CEC). David Gemmill of CE-CERT, using calibration equipment independent of that used in the CEC system performed the audit. The calibration equipment consisted of a zero air generator, a CSI Model 1700 gas dilution system, and an EPA Protocol cylinder, CC40132, certified to contain 49.3 ppm NO. The audit covered the following areas:

- 1. Calibration Accuracy.** The calibration accuracy of each analyzer's NO and NO_x channels was assessed by delivering five or six different concentrations of NO generated by the audit dilution system. The multipoint comparison data for each channel were used to generate a linear regression equation in the form: $y = mx + b$, where x is the audit concentration and y is the corresponding reported system concentration. The target data quality objective for accuracy specified in the project Quality Assurance Project Plan (QAPP) was a slope in the 0.950 to 1.050 range ($\pm 5\%$).
- 2. NO₂ Converter Efficiency.** The NO₂ converter efficiency (CE) of selected analyzers was checked by introducing known amounts of NO₂ during the multipoint audits by means of the gas phase titration procedure. Although not specified in the QAPP, the target satisfactory criteria per the regulations for source monitoring is 90% or greater.
- 3. Analyzer Precision and Response Time.** The precision of each analyzer and its response time was measured by first introducing 7.97 ppm NO to each analyzer (0.200 ppm for the low range analyzer) and recording the stable response from each channel. Then the remaining audit concentrations were introduced. At the end of the audit, zero air was again introduced. After a steady response from each analyzer was recorded, the initial high concentration was again introduced to each analyzer. The time for each channel to reach 95% of its final, stable response was measured. If this time was five minutes or less the channel was considered to have passed the test. The second stable response for each channel at this concentration was recorded and compared to the responses obtained at the beginning of the audit. The criterion for satisfactory precision is $\pm 2\%$, as described in the project QAPP.

The audit results are presented in the following table. The calibration accuracy and converter efficiency tests yielded satisfactory results for all analyzers. Using the audit slope values as a criterion, 11 of the 12 channels were within the $\pm 5\%$ range. In addition, all analyzers passed their response time and precision tests with the exception of analyzer # 4. However, it should be noted that this audit was performed after all the experiments for the CEC project had been finished.

It can be concluded that with the exception of analyzer #4, the accuracy, precision, response time, and NO₂ converter efficiency for all NO/NO_x analyzers were satisfactory, and met all the data quality objectives specified in the project QAPP.

Analyzer	DAS Channel	Range	Analyzer Channel	Slope m	Inter. b	NO₂ CE, %	Response Time Test	Precision Test
#1 TECO 42	0	High	NO	1.118	0.404		Pass	Pass
#2 TECO 42	1	High	NO	1.016	-0.007		Pass	Pass
#2 TECO 42	2	High	NO _x	0.989	-0.066	97.2	Pass	Pass
#3 TECO 42C	3	High	NO	0.950	0.020		Pass	Pass
#3 TECO 42C	4	High	NO _x	0.950	0.015	97.8	Pass	Pass
#4 TECO 42	5	High	NO	0.932	-0.364		Fail	Fail
#4 TECO 42	6	High	NO _x	0.945	-0.305		Fail	Fail
#5 TECO 42C	7	High	NO (NH ₃)	0.942	0.009		Pass	Pass
#5 TECO 42C	8	High	NO _x (NH ₃)	0.935	0.010		Pass	Pass
#6 TECO 42C	12	Low	NO	0.985	0.000		Pass	Pass
#6 TECO 42C	13	Low	NO _x	1.000	0.002	98.5	Pass	Pass