

Evaluation of NO_x Flue Gas Analyzers for Accuracy and Their Applicability for Low-Concentration Measurements

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ABSTRACT

The requirements of the Texas State Implementation Plan of the U.S. Clean Air Act for the Houston-Galveston Ozone Nonattainment Area stipulate large reductions in oxides of nitrogen (NO_x) emissions. A large number of sources at Dow Chemical Co. sites within the nonattainment area may require the addition of continuous emission monitoring systems (CEMS) for online analysis of NO_x, CO, and O₂. At the outset of this work, it was not known whether the analyzers could accurately measure NO_x as low as 2 ppm. Therefore, NO_x CEMS analyzers from five different companies were evaluated for their ability to reliably measure NO_x in the 2–20 ppm range. Testing was performed with a laboratory apparatus that accurately simulated different mixtures of flue gas and, on a limited basis, simulated a dual-train sampling system on a gas turbine. The results indicate that this method is a reasonable approach for analyzer testing and reveal important technical performance aspects for accurate NO_x measurements. Several commercial analyzers, if installed in a CEMS application with sampling conditioning components similar to those used in this study, can meet the U.S. Environmental Protection Agency's measurement data quality requirements for accuracy.

INTRODUCTION

At the time of this writing, the Texas State Implementation Plan of the U.S. Clean Air Act required 90% reduction of oxides of nitrogen (NO_x) from industrial sources in the eight-county area surrounding Houston.¹ The Dow Chemical Co.'s plan for compliance includes the application of continuous emission monitoring systems (CEMS) or predictive emission monitoring systems (PEMS) to a

IMPLICATIONS

NO_x analyzers stable and sensitive enough to measure levels of NO_x between 2 and 20 ppm are currently available. Loss of NO₂ in the NO_x analyzer sampling system is unlikely if the system is properly designed. Acceptable accuracy performance can be achieved through technically sound overall system design and analyzer selection.

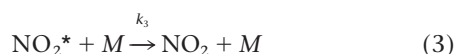
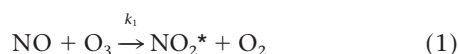
large number of NO_x sources. At the outset of this study, it was not known whether NO_x could be accurately measured at concentrations less than 10 ppm. The specifications for accuracy of NO_x measurements are defined in U.S. Environmental Protection Agency (EPA) Performance Specification 2.² In short, this specification requires that the NO_x CEMS analyzer results and all system variability be within 20% of the reference method during a relative accuracy test audit (RATA). It also requires that the NO_x CEMS analyzer not drift more than 2.5% of its span value in a single day for seven consecutive days. Because a large number of new CEMS were to be specified, an informal review of the current industrial practices was undertaken to determine the seriousness of the measurement problem. No recent peer-reviewed publications or case studies were available to assist in a simple assessment of whether low levels of NO_x could be measured in flue gas or which suppliers made technically acceptable equipment. The purpose of this study was to confidently select the analyzer technology that would meet the needs of Dow Chemical.

HISTORICAL BACKGROUND AND THEORY

Much of the current information available in textbooks regarding NO_x analyzers is based on older studies and references. For the purposes of historical perspective and to pull together information from different sources impacting this study, this knowledge is included here with appropriate referencing. In discussions with practitioners over the last three years, we realized that some of the historical information has been forgotten. The information presented in this section is not new; it provides good background and a basis for the current problems in low NO_x measurement. The use of critical orifices in instrumentation, the combustion kinetics for NO₂ formation, and the impact of converter tube temperatures on NH₃ measurements cannot be found in a single source anywhere. These are all significant considerations for low NO_x measurements.

Chemiluminescence is the most common type of NO_x analyzer. In fact, EPA reference method 7E³ currently requires a chemiluminescence analyzer. The technology

is based upon the reaction of O₃ with NO to form NO₂ in an excited state.^{4,5} From reference 4, the important reactions in a chemiluminescent detector are



In the first reaction, O₃ reacts with NO to form excited nitrogen dioxide (NO₂*). This NO₂* reaches equilibrium either through chemiluminescence (reaction 2) or through collisional energy transfer with any third body, M (quenching, reaction 3). The species and concentration of M determines the amount of quench. Therefore, the overall intensity, I, can be described as

$$I = \frac{k_1 k_2 [\text{NO}][\text{O}_3]}{k_2 + \sum_M k_{3M}[M]} \quad (4)$$

where k_{3M} is a function of the specific third body. It can be seen in eq 4 that if k_{3M} or M are small and [O₃] is much larger than [NO], then the intensity of the chemiluminescence is only a function of the [NO]. This is achieved in modern chemiluminescence analyzers through decreasing the collisional probability of the third body by operating the reaction chamber at a reduced pressure and using critical orifices to maintain a constant flow ratio of sample to O₃. A critical orifice operates at the velocity of sound such that any changes in downstream pressure do not change the flow rate of gas through the orifice. Both H₂O and CO₂ are significant quench bodies that reduce the NO response by 4.75–3.43% per mol % H₂O and 1.05–0.896% per mol % CO₂ relative to N₂.^{5,6} A typical chemiluminescence analyzer is shown in Figure 1.

NO_x is measured because NO₂ is in equilibrium with NO in the presence of O₂. Directly out of the combustion zone where the temperature is the highest, NO is the predominant species unless the gas is quickly cooled, in which case NO₂ will predominate.⁵ At cooler temperatures, NO₂ is favored. To manage these issues, NO_x, the sum of NO plus NO₂, is measured. In reporting mass, NO_x is calculated as NO₂. To measure NO₂ and NO, a converter tube in the analyzer converts the NO₂ to NO. There are several catalysts available for this conversion; stainless

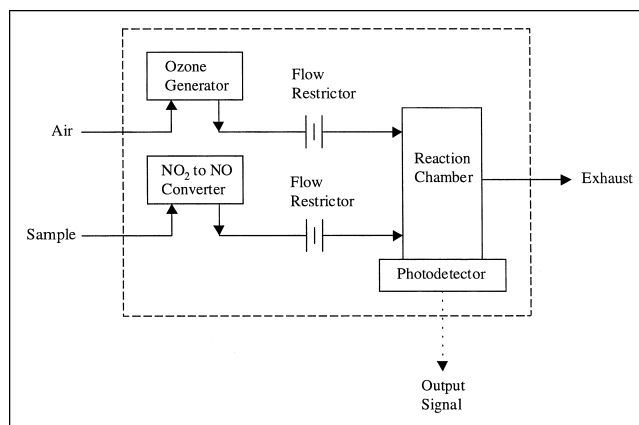
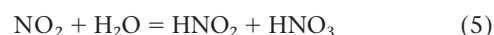


Figure 1. Typical chemiluminescence analyzer.

steel, Mo, vitreous C, and Mo coated on vitreous C are some of the more common choices. At higher converter tube temperatures, NH₃ will be converted to NO and can cause a positive bias in the NO_x measurement. This is an important consideration when NH₃ is expected in the flue gas, such as when nonselective catalytic reduction or selective catalytic reduction (SCR) units are employed to chemically minimize NO_x. At lower converter tube temperatures, the potential for conversion efficiency to decrease exists, resulting in an erroneously low NO_x measurement. Reaction temperature, however, should not be the sole consideration in selecting a NO_x converter; side reactions, efficiency, and durability should also be considered. A properly selected and designed NO_x converter should produce acceptable conversion efficiency.

Each of the analyzers evaluated in this paper measure NO rather than total NO_x. To get a NO_x reading, the NO₂ in the sample must be converted to NO by passing the sample over a heated catalyst. Different types of catalysts are available, each with certain advantages. None of the suppliers used high-temperature stainless steel, apparently because it converts NH₃ to NO and would give false high readings in an SCR-based system. Horiba uses a combination Mo/vitreous C catalyst. The California Analytical analyzer uses a proprietary low-temperature (200 °C) vitreous C catalyst, which has high efficiency and low replacement cost. Rosemount uses vitreous C. The ABB and Siemens analyzers use Mo catalyst.

NO_x is measured on a dry basis for low concentration applications. Condensed water in the sample lines decomposes the NO₂ to form HNO₂ and HNO₃.



NO₂ is very water-soluble; it decomposes as described in the previous reaction. However, NO has limited solubility: 7% at 0 °C and insoluble at 100 °C. An additional measurement problem with water was the previously

mentioned third body effect. The water problem was partially solved by selectively removing it via a “cold-finger” or impinger or, alternatively, with a Perma Pure dryer. The Perma Pure dryer is a tube and shell arrangement of acid-treated Nafion polymer. It is a highly water-permeable, desiccant-like material. On the tube side, flue gas has a high water concentration. On the shell side, the same gas, or another gas, is at a much lower partial water pressure, thus providing the necessary chemical potential to drive the water across the polymer wall. The Perma Pure dryer was shown to absorb and release NO_2 and may, therefore, not be useful for accurate low NO_x measurements.⁷ Therefore, this kind of dryer was not used in this investigation even though recent claims suggest that it is a suitable material.

Many CEMS today use Peltier-type devices to cool the sample stream in a short zone to reduce the contact time of NO_2 with the water. The condensed water is continually pumped out of the bottom of this device. Normally, the temperature of the Peltier cooler is maintained at 2–4 °C, which corresponds to a maximum concentration of less than 0.8% water, thus minimizing the quench effect, extending the lifetime of the NO converter, and protecting the analyzer from water condensation.

The CO_2 quench is less significant than the H_2O quench and is managed differently. Chemiluminescence technology is extremely sensitive and able to detect part per trillion concentrations of NO. A commercially available chemiluminescence NO_x analyzer is essentially “detuned” by using less gain on the optics and less sample in the analyzer, along with other appropriate engineering modifications. As a result, commercially available chemiluminescence NO_x analyzers currently offer a minimum measuring range of 0–2 ppm. The more sensitive analyzers may operate with a higher ratio of sample to O_3 than the less sensitive analyzers. However, this increase in sensitivity comes at the expense of an increase in the third body quench. It turns out that a modern analyzer designed with a detection limit of 0.1 ppm will have a CO_2 quench that is so small that it does not significantly impact the accuracy of the NO_x measurement, whereas an analyzer designed with a detection limit of 0.02 ppm will be impacted. The EPA methods permit calculation of this effect in the results reporting, but it adds an uncertain step in data processing that most users wish to avoid.

An entirely different approach to overcoming the NO_x quench problem has been taken by some users, particularly those with high particulate loading and SO_2 . These users prefer to use a dilution system, which splits the flow of the flue gas at a controlled ratio of, for example, 100:1. This approach has been developed to lower the concentration of interfering and potentially corrosive substances in the analyzer. However, dilution presents a

challenge to accurate measurements. This was outlined in the EPRI CEMS Analyzer Bias and Linearity Effects study.⁸ Because there are so many variables involved with making this approach work, the decision was made to not use it. Dilution requires more hardware and, in Dow flue gas applications in Texas, would require more maintenance, including dilution gas usage. In addition, employing dilution requires more complicated software control and higher user training and expertise.

Another early approach that deserves mention but did not turn out to be historically successful was a chemiluminescence method that does not require an NO converter. It instead relies on the reaction of NO and NO_2 with H_2 that has been generated through electrical discharge.⁹ It is likely that interference and mechanical complexity caused this technique to fail in commercial applications. Yet another approach involves IR absorbance. This approach has been used with reasonable success, but currently the lowest range of the technology is 0–50 ppm, too high for our application requirements. Several companies market IR analyzers.

An alternate to the chemiluminescence method is differential UV. ABB offers a differential UV absorbance analyzer that determines NO.¹⁰ A converter tube is used to convert NO_2 to NO, similar to the chemiluminescence type analyzers. The light source is an electrodeless discharge lamp (EDL), which uses high-frequency induction in an atmosphere of N_2 and O_2 to create a plasma. The plasma gives some select emission lines for NO; 226 nm is selected by an interference filter. The spectrum is shown in Figure 2. The optical bench of this analyzer is shown in Figure 3.

Measurement stability is obtained with a four-beam optical method that uses either a clear or an NO-filled gas cuvet to block NO specific absorption and a beam splitter with a reference detector. This method allows for

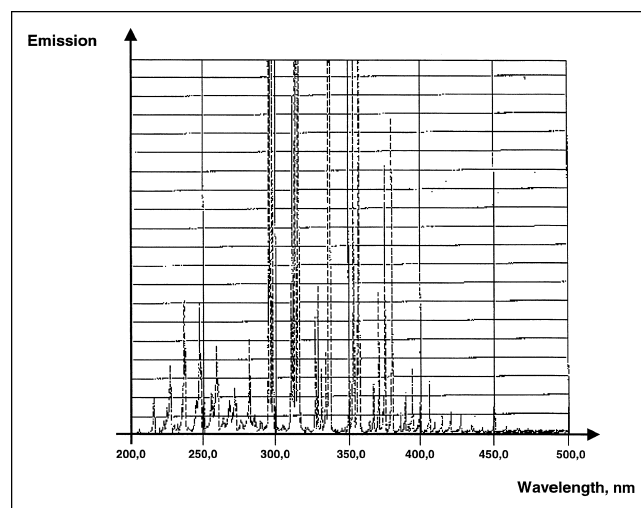


Figure 2. Plasma emission from N_2 and O_2 EDL.

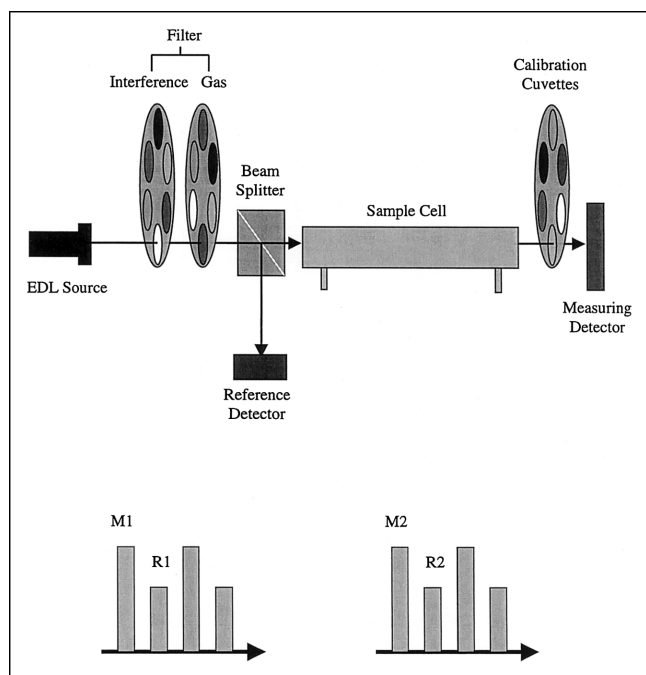


Figure 3. Optical bench and measurement modes for ABB LIMAS differential UV analyzers.

compensation of source and detector aging and also for contamination or fouling of the sample cell. There are four intensity measurements, R1, R2, M1, and M2, as shown in Figure 3. R1 is the measurement of the source intensity when the filter wheel is open. R2 is the measurement of source intensity when the filter wheel contains a cuvette with NO, thus blocking specific NO wavelengths. M1 is the intensity of the source less that absorbed by gas in the sample cell. M2 is the intensity of the source less that absorbed by the NO gas filter and nonspecific absorbance in the sample cell. M1 and M2 are separated in time, as are R1 and R2. The absorbance caused only by the analyte, NO, in the sample cell is thus

$$A = \frac{\frac{R1}{M1} - \frac{R2}{M2}}{\frac{R1}{M1}} \quad (6)$$

Another feature of this analyzer is the ability to calibrate without a flowing gas. The calibration wheel contains gas-filled cuvettes, which, when rotated into the optical path, are equivalent to an absorbing gas in the sample cell and are thus useful for calibration. The lowest measurement range available is 0–5 ppm, which is likely to be more sensitive than is necessary. Differences between differential UV and chemiluminescence measurement of NO_x are summarized in Table 1.

One promising technology is in situ analyzers. These units have no sample extraction or sample conditioning

systems. Currently, Procal and Sick Optic manufacture such units. They consist of a porous metal tube, which acts as a filter. This metal tube is installed inside the process pipe or vessel. The NO_x that penetrates the tube is measured in the IR (high-level measurements; e.g., 50–200 ppm) or UV (low-level measurements; e.g., 0–20 ppm) range. The products differ in their multivariate statistical algorithms used to selectively determine the specific concentration of NO and NO₂. The overall system is greatly simplified because the analyzer and electronics mount directly on the stack; there is, therefore, no sample conditioning system or analyzer house required. Although this approach has the potential to save considerable cost, it was not evaluated here because the companies are not well represented in the United States (service could be a problem), the technology is too new for a large number of installations, and maintenance personnel do not favor having to climb a stack to maintain an analyzer.

The future of NO_x measurement technology will likely be advanced through sensor development for the automotive industry. Every new car may have a NO_x sensor in the coming years. These sensors are currently under development at various institutions and are based on electrochemical, surface plasmon resonance, surface acoustic wave technology, and other mechanisms.

CHALLENGES FOR LOW NO_x MEASUREMENTS

During the last 10 years, analyzer manufacturers have significantly increased the maintenance reliability of CEMS NO_x analyzers. At the same time, regulations have required much lower measurement concentrations to the point that measurements less than 15 ppm are considered to be low NO_x measurements. There are three economic drivers for having accurate measurement technologies: (1) process control, (2) NO_x trading credits, and (3) the ability to certify accuracy to effectively give the operating unit the “license to operate.” Accurate NO_x measurements allow the combustion sources to be optimized for power

Table 1. Differences between differential UV and chemiluminescence measurement of NO_x.

	Chemiluminescence	Differential UV
Method	Chemical	Spectroscopic
Ozone generator	Yes	No
Quenching effects	Yes	No
Auxiliary gas (air or O ₂)	Yes	No
Deozoneizer	Yes	No
Vacuum pump	Yes	No
Converter	Yes	Yes
Calibration	Flowing gas	Internal cuvettes or flowing gas
Dynamic range	1000 (e.g., 10–10,000 ppm)	500

output versus NO_x concentration or to minimize NH_3 reagent usage in SCR units. NO_x credits are based on “Cap and Trade” agreements. An industrial source will be permitted to emit no more NO_x than a previously defined emission limit. If the source emits under this cap, it has NO_x credit that it can sell through a brokerage to another source that is over its cap. Being under the limit could produce substantial revenues. The “license to operate” implies that the operating unit’s CEMS (or PEMS) is certified to produce accurate data during a RATA and, thus, the unit is allowed to continue operation.

The main technical challenge in this work was to establish whether a CEMS NO_x analyzer could reliably make accurate measurements in the 2–20 ppm range. For a CEMS NO_x analyzer to achieve this (1) there should be no measurement bias caused by the sampling system or by quench effects, (2) the drift should be within EPA Performance Specification 2 guidelines, and (3) the concentration resolution for measuring NO_x should be significantly less than the expected NO_x levels in the sources (2.5 ppm), to allow for adequate measurement confidence. A 5% error in a CEMS with a range of 0–10 ppm would mean a 0.5-ppm error in the NO_x concentration, effectively challenging the 20% accuracy requirement of a RATA for a low NO_x source. Potential errors investigated included converter efficiency, loss of NO_2 in the sample conditioning system, CO_2 quench, and third body effects related to the calibration of the analyzer in a dry N_2 matrix while running the analyzer in an entirely different matrix stream.

EXPERIMENTAL PROCEDURES

NO_x Analyzers Selected for Evaluation

Two previously completed studies on low-level CEMS NO_x analyzers served as screens for selecting such analyzers for this evaluation; one study was completed by General Electric Energy and Environmental Research,¹¹ the other by the University of California–Riverside.¹² Based on our review of these studies, NO_x analyzers from five suppliers were selected: Horiba Instruments, Inc.; California Analytical Instruments (CAI), Inc.; Rosemount Analytical, Inc.; ABB Automation, Inc.; and Siemens Applied Automation, Inc.

Testing Apparatus

The testing apparatus used to evaluate the NO_x CEMS analyzers is shown in Figure 4. It was designed to meet the three major objectives of simulating an actual NO_x source with precise control of components and compositions, providing sample conditioning similar to a typical CEMS installation, and simultaneously testing all the analyzers.

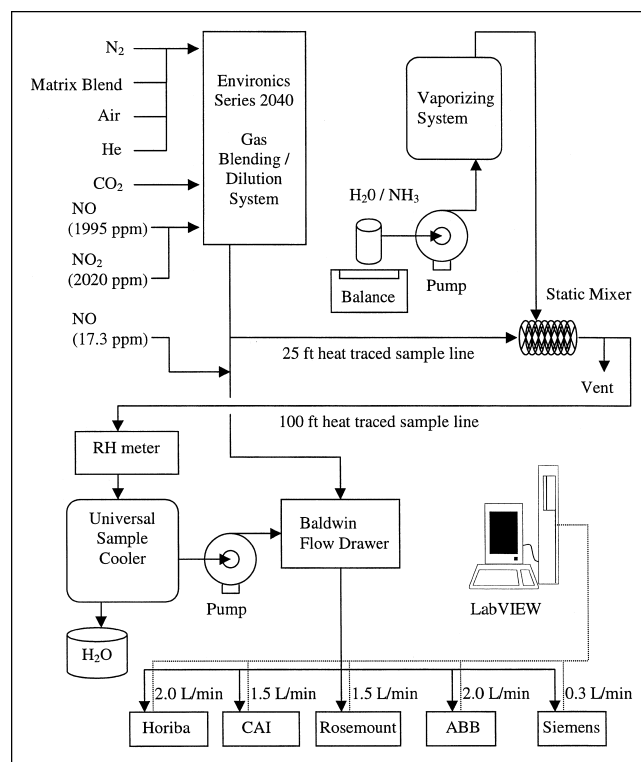


Figure 4. NO_x analyzer testing apparatus.

NO_x Source. The NO_x source synthesized in the laboratory contained components typically found in flue gas. NO and NO_2 were diluted with blends of N_2 , CO_2 , O_2 , air, and, at times, He . This gas was preheated and then mixed with water vapor and NH_3 . To precisely control the components, an EnviroNics Series 2040 computerized multi-component gas blending/dilution system was used to blend the diluent (dilution) gases with the NO and NO_2 . The gas blending/dilution system uses multiple mass flow controllers to generate a gas blend of a specified concentration and flow rate.

Various gases and gas blends were used as the diluent gas. Zero-grade N_2 cylinder gas was used for zero and span calibration of the analyzers. A Scott Master Class Accublend gas cylinder of 14.95% CO_2 , 3.03% O_2 , and N_2 balance was used as a matrix-blend diluent gas. Zero-grade air was used to dilute instrument-grade CO_2 during the chemiluminescence quenching test.

NO and NO_2 gas standards were chosen in the 2000-ppm range so that their addition was small relative to the diluent gas flow rate. This allowed for changes in the NO or NO_2 concentrations that did not significantly change the matrix. The NO_2 standard used was a Scott Certified Master Class gas cylinder at 2020 ppm in N_2 . The NO standard used was a Scott Certified Master Class gas cylinder at 1995 ppm in N_2 . This standard was diluted to 17.3 ppm with N_2 by the EnviroNics system to calibrate the analyzers. A Scott RATA Class Calibration Standard

NO gas cylinder at 17.3 ppm was chosen to verify the Master Class standard and the dilution system.

The output from the Environics was valved for flow either directly to the analyzers, via the flow drawer, or through the sampling system. Flow was valved directly to the analyzers for zero and span calibration. For the sampling system, the blended gas was preheated to 120 °C through 25 ft of heated tetrafluoroethylene (TFE) tubing. At this point, water vapor was injected. The water vapor was generated by pumping water through heat-traced 1/8-in. copper tubing, through a heat-traced 500-mL type 316 stainless-steel (316 SS) cylinder, and then through heat-traced 1/16-in. tubing. The cylinder helped dampen the flow fluctuations caused as the water flashed within the hot tubing. The water addition was calibrated gravimetrically with a Mettler PC 2000 analytical balance. For NH₃ addition, NH₄OH was added to the water. A Kenics static mixer (0.38-in. tube 316 SS with 21 elements) immediately following the water vapor injection provided the final mixing of this NO_x source. The flow from the Environics dilution system was controlled at two rates. Flow was set at 8000 mL/min when the output was valved directly to the Baldwin flow drawer and at 9000 mL/min when the output was valved to the sample system. The higher rate provided excess sample to the sample system.

Sample Collection. From the output of the static mixer, the sample was collected as though it was from an actual NO_x emissions source. A 100-ft heated TFE sample line, previously used for stack gas sampling, was connected to a tee downstream of the static mixer tube. The tee was connected to a valve to provide a vent for excess sample. The heated sample line was temperature controlled by a Clean Air Engineering controller at 120 °C. The output of the sample line was connected to a sample conditioner. A Vaisala relative humidity sensor (HMP230) was inserted before the conditioner. The sample conditioner consisted of a Universal Analyzers Model 3080 SS sample cooler (maintained at 4 °C) and an Air Dimensions DIA-VAC Model 19310T vapor pump. Conditioned sample was pumped to a Baldwin Environmental BEI Model 3300 flow-control drawer.

Analyzers. The Baldwin flow-control drawer distributed conditioned sample to the analyzers in parallel. This arrangement allowed for simultaneous testing of all the analyzers. Recommended flow rates were controlled for each individual analyzer. The sample pressure at the flow drawer was approximately 11 psig. This pressure was maintained whether the sample arrived directly

from the Environics dilution system or through the sample system. The flows to the analyzers were

- (1) Horiba CLA-510SS 2 L/min
- (2) CAI 400 HCLD CE 1.5 L/min
- (3) Rosemount CLD 194006 1.5 L/min
- (4) ABB LIMAS 11 CEM 2 L/min
- (5) Siemens CLD 70SE 0.3 L/min

All of the analyzers used NO_x converters. The range was set at 0–20 ppm for all of the analyzers except the CAI, which was set at 0–30. The CAI was an analog device, with preset selectable measuring ranges; 0–30 was the lowest selectable range on the analyzer. The output analog signals were transmitted to a LabVIEW program on a desktop computer for data collection and logging into an Excel spreadsheet.

RESULTS AND DISCUSSION

Experimental System Validation

Gas blends created with the blending system had a specified accuracy of ±2%. To confirm the accuracy of the blended gases, a 17.3-ppm gas cylinder standard was compared with a blended standard of 17.3 ppm that was created from a 1995-ppm calibration gas. The data in Table 2, averaged over a 4–5-min period of measurement, confirmed the accuracy of the blending system. All diluted measurements were less than 1% different than the undiluted reference gas.

Check for Measurement Interferences

Figures 5 and 6 show the effect of CO₂ on the analyzer readings at constant NO and NO₂ levels. With the exception of the ABB analyzer, the presence of CO₂ caused some negative interference with the NO_x analysis. The ABB UV analyzer was not expected to show CO₂ interference because CO₂ does not have UV absorbance at 226 nm. The test data, shown in Figure 5, confirm this expectation. Most of the chemiluminescence analyzers showed acceptable performance with respect to CO₂ interference, indicating that the analyzers had been designed to minimize this effect. The one exception was the Siemens analyzer. This analyzer was reportedly designed to achieve lower detection limits than the other analyzers by introducing a larger mixing ratio of sample to O₃ in the reaction chamber. The result was a higher sensitivity to CO₂ quenching. As shown in Figures 5 and 6, the NO and NO₂

Table 2. Blended standard gas vs. gas cylinder standard gas.

	Horiba	CAI	Rosemount	ABB	Siemens
Average reading on blended 17.3 ppm standard (ppm)	17.5	17.6	17.5	17.5	17.3
Average reading on gas cylinder 17.3 ppm standard (ppm)	17.4	17.4	17.4	17.4	17.4
Difference (%)	0.68	0.88	0.49	0.64	-0.13

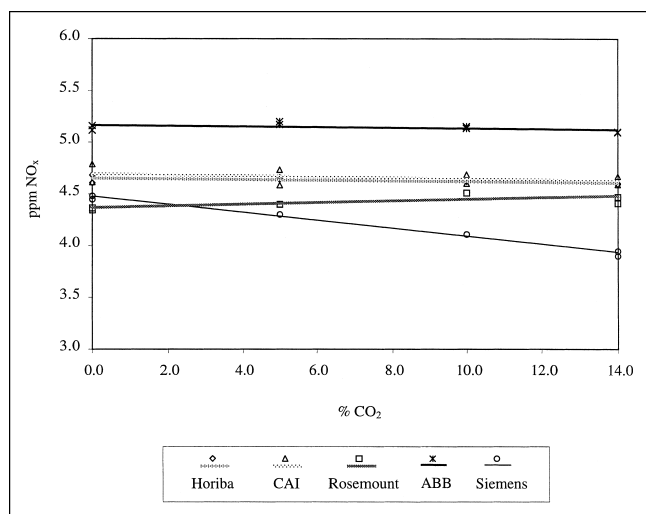


Figure 5. CO₂ effect on NO_x analysis (5 ppm NO).

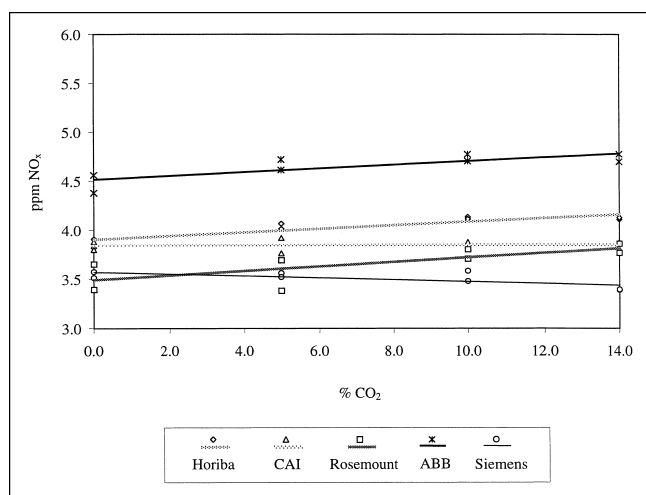


Figure 6. CO₂ effect on NO_x analysis (5 ppm NO₂).

analyses for the Siemens analyzer indicate a downward trend with increasing CO₂ in the diluent gas (water composition was constant, nullifying NO₂ absorption effects). Interference levels or quenching effect from CO₂ were calculated on a % NO_x quench per % CO₂ basis; the results are summarized in Table 3.

Interference Particular to the ABB Analyzer

Because the ABB UV source produces O₂ emission lines, there is a small sensitivity to O₂ in the sample. Figure 7

Table 3. CO₂ interference on NO_x readings at 5 ppm NO.

	Horiba	CAI	Rosemount	ABB	Siemens
% NO _x quench per % CO ₂ for 0% CO ₂	0	0	0	0	0
% NO _x quench per % CO ₂ for 5% CO ₂	-0.02	0.18	-0.20	-0.18	0.73
% NO _x quench per % CO ₂ for 10% CO ₂	0.05	0.12	-0.35	-0.01	0.79
% NO _x quench per % CO ₂ for 14% CO ₂	0.07	0.11	-0.14	0.05	0.86
% average NO _x quench per % CO ₂	0.03	0.14	-0.23	-0.04	0.79

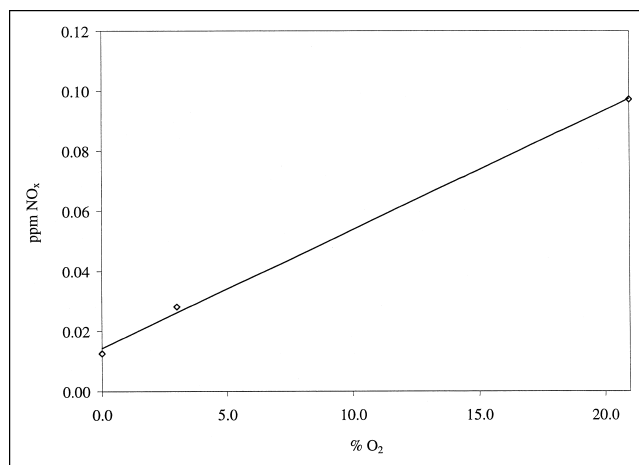


Figure 7. Effect of O₂ on ABB UV NO_x analyzer.

shows this effect. This effect applies only to the UV analyzer and not to the analyzers that use chemiluminescence detection. As long as the NO_x concentration is greater than 4 ppm, the error of this effect is less than 2% of measurement and does not need to be corrected in the data collection system. In a later version of this analyzer, a new interference filter had been selected that the manufacturer claimed reduced this O₂ response by a factor of 5.

Analytical Precision, Accuracy, and Linearity

Linearity and estimated detection limits for the analyzers are summarized in Table 4. The detection limit was estimated by multiplying the SD (or noise level) of the zero gas readings during five different experiments by 3.¹³ Table 4 and Figures 8 and 9 show the results of the linearity testing for NO and NO₂.

All the instruments showed excellent linearity and satisfactory detection limits. A satisfactory detection limit is less than 2% of span. All of the analyzers had a 20-ppm span with the exception of the CAI, which had a 30-ppm span. Table 4 shows that all five analyzers demonstrated detection limits that were less than 2% of span and that the noise levels were within acceptable levels. The data collection system logged data to the nearest 0.1 ppm, so the detection limits reported here may be somewhat conservative. The average reading for the ABB analyzer on zero gas was 0.2 ppm. This effect resulted because a poorly designed prototype sample cell in the analyzer required an extraordinarily long time (more than 10 min) to satisfactorily purge the cell; because of inadequate purging, there were traces of NO_x remaining in the cell when running the zero gas samples.

As Figures 8 and 9 indicate, four of the five analyzers exhibited excellent linearity. The Siemens analyzer gave acceptable linearity, although it showed the greatest deviation from unity on

Table 4. Estimated NO_x detection limits and linearity.

	Horiba	CAI	Rosemount	ABB	Siemens
Estimated detection limit (ppm)	<0.1	<0.1	<0.1	<0.1	<0.1
Slope	0.956	0.956	0.962	0.968	0.812
Intercept	0.0944	0.1306	0.1291	0.2460	0.0793
Regression coefficient	0.9999	0.9998	0.9999	0.9999	0.9998

the slope, apparently because of CO₂ quenching. It is interesting to note that the estimated detection limit for the Siemens analyzer was not significantly better than that of the other analyzers, even though the poor CO₂ interference rejection was stated to be caused by a design that gave superior detection limits.

It is important to have a high converter efficiency so analysis errors are minimized, particularly for low levels of NO₂ (e.g., 5 ppm). Table 5 shows the converter

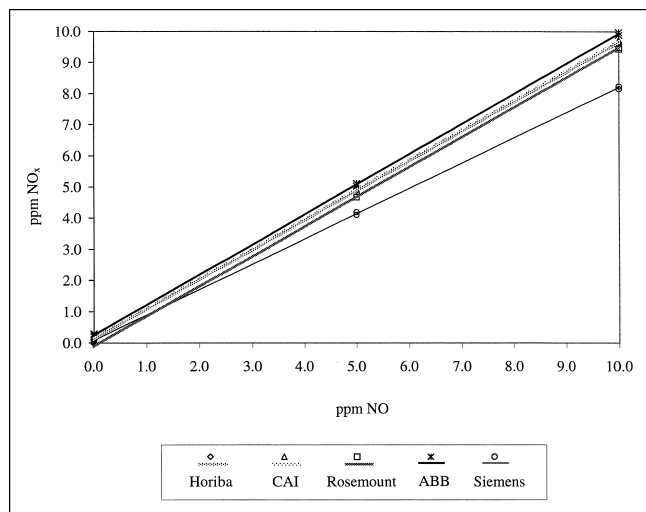


Figure 8. NO linearity (NO_x reading vs. NO concentration).

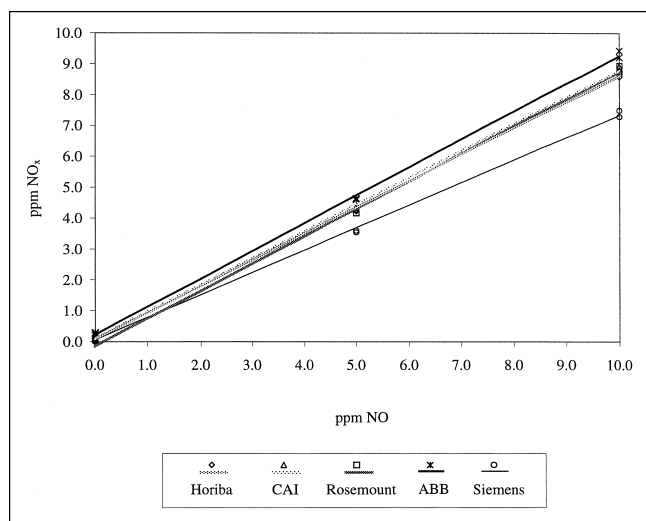


Figure 9. NO linearity (NO_x reading vs. NO₂ concentration).

efficiency at 0 and 15% CO₂ for the various analyzers. At low CO₂ concentrations, the converter efficiencies ranged from approximately 90 to 95%. At 15% CO₂, the measured converter efficiencies were lower, possibly because of the reduction in sample O₂ concentrations that resulted from the blending of the CO₂ with our air mixture. The effect of converter efficiency versus O₂ concentration or

water content was not investigated. All the analyzers tested came equipped with NO_x converters. Following span calibration, the NO_x converter performances were verified by measuring NO₂ diluted in N₂. In the experimental design, the analyzers were tested as a unit, consisting of the analyzer with the converter. Therefore, the effects of O₂ concentration or water content on NO and NO₂ were attributed to the analyzer unit and not isolated for the individual converters.

To determine the bias introduced as a result of NH₃, samples with 10-ppm NH₃ were prepared. Table 6 shows the effects of the NH₃ on NO and NO₂ samples. Basically, there was no significant effect from NH₃. Ammonia was detected in the condensate from the sample cooler, indicating that the cooler was scrubbing NH₃ from the matrix. Perma Pure manufactures an NH₃-scrubbing sampling system cartridge. The device was tested and was found to effectively remove NH₃ from the sample stream, as indicated by the fact that there was not a false high NO_x reading. At 10-ppm NH₃, the NO recovery averaged 101% and the NO₂ recovery averaged 99%.

Another potential source of error in the measurement of NO_x is the loss of NO₂ in the water-removal stage. Gas blends with and without water were generated to see if there was any difference between the measured NO_x values. Table 7 shows that the NO₂ losses were less than 2%, which is within the error of the experimental system. The large error in the Siemens analyzer results is likely caused by a higher sensitivity to water quenching.

Drift

As specified by EPA Performance Specification 2, the drift of the NO_x CEMS analyzer must be less than 2.5% of full span per day, measured daily for seven consecutive days on both zero and span gas. Recalibration is permitted

Table 5. NO₂ converter efficiencies at 0 and 15% CO₂.

	% NO ₂ Converted to NO				
	Horiba	CAI	Rosemount	ABB	Siemens
Dry sample with 0% CO ₂	89.6	89.4	95.3	93.9	94.9
Dry sample with 15% CO ₂	88.5	90.3	91.5	92.2	88.8

Table 6. Effect of NH₃ on NO_x measurements.

	% Recovery with 10 ppm NH ₃ in Sample Calculated as (measurement with 10 ppm NH ₃)/ (measurement without NH ₃)				
	Horiba	CAI	Rosemount	ABB	Siemens
10-ppm NO in matrix of 15% CO ₂ , 3% O ₂ , 15% H ₂ O, balance N ₂	100	100.9	94.9	100.3	97.5
10-ppm NO ₂ in matrix of 15% CO ₂ , 3% O ₂ , 15% H ₂ O, balance N ₂	95.6	96.2	91.5	96.3	96.5

every day. The span gas is typically at 80% of the span range for the measured component. The zero drift for the analyzers is listed in Table 8 for a period of five days in the laboratory without calibration.

The drift of the ABB was biased high because of inadequate flushing of residual NO. (This was a design flaw that was later fixed.) In all cases, the zero drift was low enough to be considered acceptable. In a further exploration of analyzer drift, the CAI NO_x analyzer was subjected to a field drift experiment in a mobile laboratory normally used for process measurements and CEMS certification. The analyzer was calibrated once and allowed to run for a week on a flue gas NO_x application. Periodically, the zero and span drift were measured but the analyzer was never recalibrated. The results are summarized in Table 9.

In all cases, the zero and span drift were well within the required guidelines of EPA Performance Specification 2. It is not appropriate to suggest that if the span were 0–10 ppm, the drift would triple because the range was reduced by a factor of 3 (specifically in the case of the CAI NO_x analyzer, which had a range of 0–30 ppm). Three times this drift would not meet the requirements of EPA Performance Specification 2. When the analyzer is spanned at a low range appropriate for the application, the noise decreases also. It is reasonable to believe that the drift would also be less, especially because all of the installations are in temperature-controlled shelters. Because testing was not completed with a lower range analyzer, it cannot be absolutely concluded that there would not be challenges in meeting the drift requirements of EPA Performance Specification 2. However, the data in Tables 8 and 9, in conjunction with good installation design, indicate that the challenges should be minimal.

Table 7. NO₂ losses caused by solubility in water.

	Horiba	CAI	Rosemount	ABB	Siemens
NO ₂ lost from 10-ppm standard (ppm)	-0.01	0.11	0.14	0.18	0.73
% NO ₂ recovered	100.1	98.9	98.6	98.2	92.6

Field Test

Two separate but similar sample trains were placed on a gas turbine. One train had a single CAI NO_x analyzer. The other train had a CAI NO_x analyzer and an ABB NO_x analyzer. The purpose of the experiment was to determine if these two different technologies gave equivalent results and how much variation should be expected between two similar analyzers. When the data were plotted in terms of relative differences, the variability indicated a difference of approximately 1% for identical manufacturers and 5% between manufacturers. Because the relative accuracy criterion for EPA Performance Specification 2 is 20%, there was no effort to determine why there was a 5% difference.

A "Worst-Case Scenario"

Understanding what was known from the laboratory and field measurements can be applied to consider some extreme conditions, specifically for the purpose of modeling the impact of a worst-case scenario and determining if the relative accuracy requirements would still be acceptable. The conditions for this worst case assumed measurement of 5 ppm NO_x, with 50% of the NO_x being NO₂. It is also assumed that 10% of the NO₂ is lost in the chiller (0.25 ppm) and there is a 0.08-ppm loss resulting from CO₂ quenching. If the converter efficiency is assumed to be only 90%, the minimum required, then there is another loss of 0.23 ppm NO_x. Finally, a calibration error of 0.25 ppm is assumed. The measured NO_x value would thus be

$$5 - (0.25 + 0.08 - 0.23 + 0.25) = 4.19 \text{ ppm} \quad (7)$$

A value of 4.19 ppm corresponds to a relative accuracy of -16%, still within the requirements of EPA Performance Specification 2.

Summary of Measurement Capabilities

The evaluation data indicated that all of the analyzers tested would be acceptable for flue gas applications. The ABB analyzer that was originally supplied had an unacceptably long response time because of an unsuitable sample cell design. An improved sample cell was supplied near the end of the evaluations, and the response time of

Table 8. Zero drift on NO_x analyzers (5 days without calibration).

	Horiba	CAI	Rosemount	ABB	Siemens
% average drift per day	0	-0.02	-0.04	-0.24	-0.05
Span (ppm)	20	30	20	20	20

Table 9. Zero and span drift deviation for CAI NO_x analyzer (without calibration).

Date and Time	Zero Drift (%)	Span Drift (%)
10/17/01 02:10	1	1.3
10/17/01 08:15	1	0
10/17/01 14:20	1	1
10/17/01 20:26	1.3	1
10/18/01 02:31	1	1
10/18/01 08:36	1.3	0.7
10/19/01 09:17	0.3	2
10/24/01 09:31	0.7	1.3

the analyzer was confirmed to be comparable to the other analyzers tested.

CONCLUSIONS

NO_x analyzers from five companies, Horiba, CAI, Rosemount, ABB, and Siemens, were selected for evaluation. All of these analyzers, with the exception of the ABB, were based on the O₃-NO chemiluminescence reaction. The ABB was based on a UV absorbance measurement using the gas filter correlation principle. The measurement capabilities of the analyzers indicated that all but the Siemens would give nearly equivalent data. The Siemens analyzer had a significant quench effect from CO₂, which caused the reported NO_x concentrations to be biased low. The ABB analyzer was found to have a small positive bias from O₂, which can be corrected in the data acquisition system if necessary. A field test was performed at a gas turbine for the ABB and CAI analyzers. The results of the test indicated that at 6–8 ppm NO_x, the maximum relative error was between 1 and 5%, well within the 20% window allowed by EPA Performance Specification 2. In addition, a worst-case scenario model for low NO_x measurements indicated that NO_x can be measured with sufficient accuracy.

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