



Investigative Results of NO_x Measurement Bias Due to CO₂ and Moisture Effects

Author:

Jack Bionda

jbionda@cleanair.com

Clean Air Engineering

1601 Parkway View Drive

Pittsburgh, PA 15205

Ph: 412-787-9130

Fax: 412-787-9138

Co-authors:

John Chapman (CleanAir)

Don Allen (CleanAir)

Mark Ambler (CleanAir)

Scott Evans (CleanAir)

Steve Rees (CleanAir)

ABSTRACT

Increasingly stringent environmental regulations have resulted in nitrogen oxides emission limits below 100 parts per million on many existing large combustion sources, and below 10 parts per million on many new sources. The question has arisen as to whether the analyzers used to document compliance with these limits are prone to a measurement bias that could result in under-reporting of actual emission rates. Clean Air Engineering conducted a laboratory investigation of four commercially available chemiluminescent NO_x analyzers to determine the potential for instrument bias due to moisture and carbon dioxide (CO₂) quenching. This paper presents the findings of the laboratory tests. CO₂ quenching was found to be a more significant contributor to instrument response bias than the effect of moisture, and this effect is more pronounced in instruments designed for low range measurements. The maximum CO₂ quenching bias found in the study accounted for approximately a 1% diminished signal for each 1% of CO₂ present in the sample gas.

INTRODUCTION

Chemiluminescent analyzers are the principal analytical technology available for determining nitric oxide (NO) emission levels from combustion sources.

Chemiluminescence describes the process of fluorescence resulting from a chemical reaction. Chemiluminescent analyzers are usually calibrated with a blend of NO in a N₂ balance. When sampling from combustion systems, additional species are encountered, including H₂O, CO₂, CO, and O₂. Under certain circumstances, the composition of the gas stream being measured can affect the measurement of NO due to differences in third body quenching reactions between the calibration gas and the sample gas. The most prevalent form of instrument response bias is a reduction in the chemiluminescence intensity by quenching in the reaction chamber due to the presence of CO₂ and H₂O.

Background

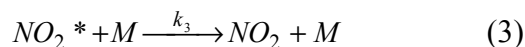
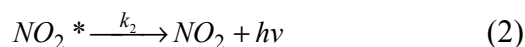
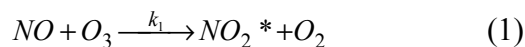
The phenomena of third body quenching of the chemiluminescence intensity in nitric oxide analyzers has appeared in the literature for at least the past twenty five years. Matthews, et al. [1] documented this occurrence in considerable detail in a paper published in 1977. The U.S EPA has been slow to address this interference bias as a possible significant source of measurement error. However, as emission limits have been ratcheted down in recent years, third body quenching and other sources of measurement bias need to be re-examined as likely contributors to inaccuracies in nitric oxide emission rates from combustion sources. The requirement for accurate and precise measurement is critical for determining compliance as well as offsets for NO_x credit trading programs, especially in a deregulated operating environment.

The U.S. EPA requires an interference response check be performed on chemiluminescent NO_x analyzers as part of a nitric oxide emission test for stationary combustion sources under Method 7E or Method 20 of CFR 40, Part 60. EPA Method's 7E and 20 call for an interference check using 10% CO₂ in a blend of O₂, CO, and SO₂ in a N₂ balance, or as an alternative, each gas can be introduced separately. However, quenching is not apparent unless there is CO₂ in the NO calibration gas. Nitric oxide calibration gas is typically NO and NO₂ in a balance of N₂. CO₂ alone (i.e. in N₂) causes little or no response from the NO_x analyzer; hence the instrument will easily pass the 2% interference response check criteria when challenged by a calibration gas that does not contain a blend of CO₂ and NO.

The process of certifying a continuous emission monitoring (CEM) system can be difficult on plants with low (i.e. single digit) NO_x emissions, particularly the requirement for a relative accuracy audit test audit (RATA). When performing a RATA of a CEM system, CO₂ quenching may be significant if the monitor being certified uses CO₂ in its calibration gas or if the effect of CO₂ quenching is accounted for in its software.

Chemiluminescent NO_x Analyzer Functionality

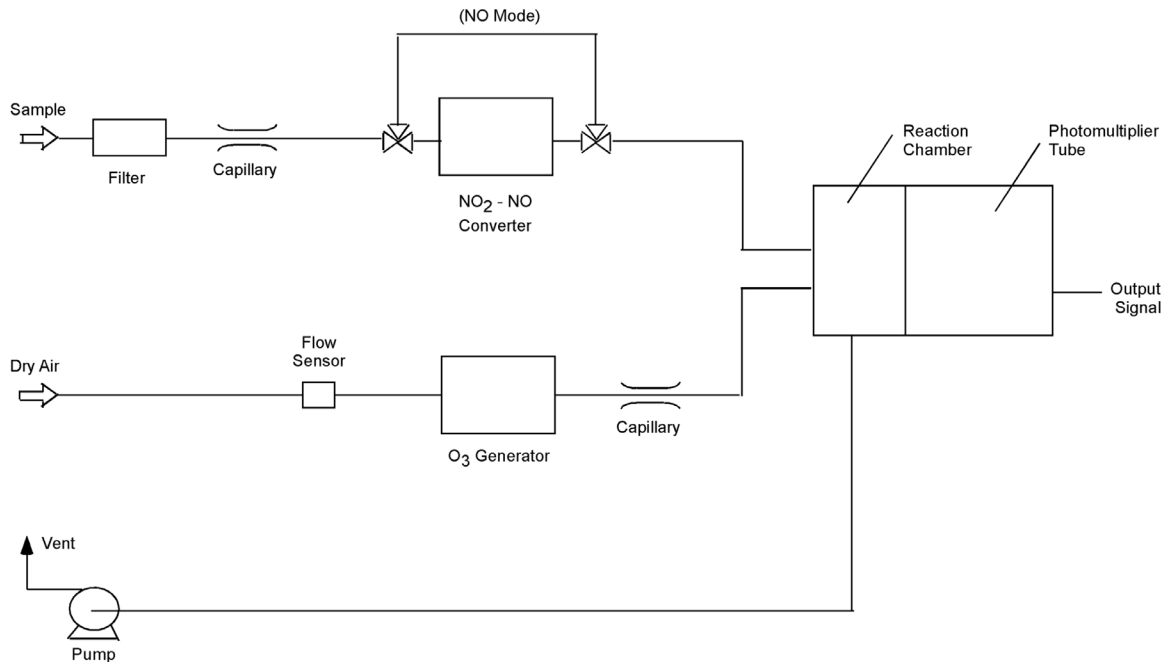
The reactions of importance in the chemiluminescent analyzer can be summarized as follows:



When NO in a gas sample reacts with ozone, nitrogen dioxide (NO₂) is generated in its electronically excited state (Reaction 1). When the generated NO₂ returns to the ground state (Reaction 2), it emits light (chemiluminescence). The concentration of NO can be determined by measuring the intensity of this chemiluminescence. NO₂ can reach equilibrium either through chemiluminescence (Reaction 2) or through collisional energy transfer (Reaction 3) to a third body (M). [1]

A generalized schematic of a chemiluminescent analyzer is shown in Figure 1. NO in a gas sample reacts with O_3 which is prepared by means of an ozone generator in a reaction chamber. The chemiluminescence generated in this reaction is detected with a photomultiplier. The intensity of NO is in direct proportion to the NO concentration in a wide concentration range. By switching a three-way valve, the sample gas is passed through a converter to convert NO_2 into NO; the concentration of NO_x (NO and NO_2) can be obtained by measuring the intensity of the chemiluminescence. The concentration of NO_2 in the sample gas can be obtained by calculating the difference between the two measured values. This analysis method is very sensitive and selective for the quantification of NO_x .

Figure 1
Chemiluminescent NO/NO_x Analyzer



EXPERIMENTAL APPROACH

Clean Air Engineering tested four (4) chemiluminescent NO_x analyzers from two (2) different manufacturers. One (1) Eco Physics and three (3) TECO analyzers were evaluated simultaneously. The manufacturer's design specifications for each analyzer are provided in Table 1. The third body quenching rate was demonstrated by dynamically mixing NO with a carrier gas comprised of various concentrations of CO₂ in an N₂ balance. Two different NO concentrations (25 and 80 ppmv) were tested in each analyzer. CO₂ concentrations of 5% and 15% by volume were assessed. The effect of passing the gas stream through a gas conditioner in order to document the effect of residual moisture was also evaluated in three of the four test analyzers.

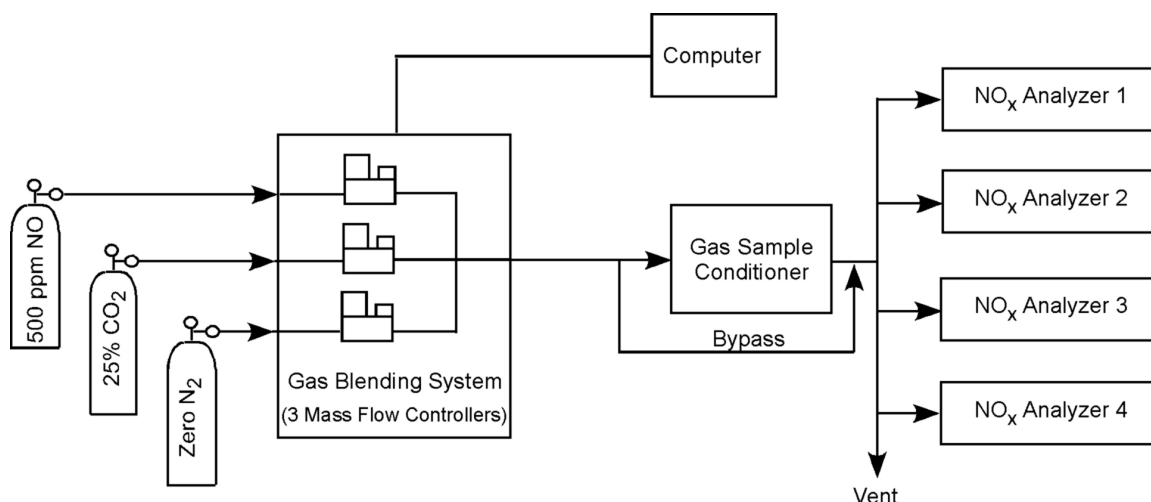
Table 1
Design Specifications of Test Analyzers

Parameter	Eco Physics Model 70E	TECO Model 42C	TECO Model 42C Low Source	TECO Model 42CHL
Range(s)	0-500 ppm; four ranges, user selectable	0-50, 100, 200, 500	0-2 ppm; 0-200 ppm	0-10, 20, 50, 100, 200, 500, 1000, 2000, 5000 ppm
Min. Detection Concentration	0.02 ppm	0.40 ppb	0.01 ppm	50 ppb
Zero Noise	0.01 ppm	0.20 ppb RMS	0.005 ppm	25 ppb
Zero Drift (24 hour)	0.1 ppm/ 6h	<0.40 ppb	0.005 ppm	50 ppb
Span Drift (24 hour)	Not Reported	±1% of full scale	±1% of full scale	±1% of full scale
Linearity	±1% of full scale	+1% of full scale	±1% of full scale	+1% of full scale
Sample Flow Rate	330 cc/min	600 cc/min	~110 cc/min	25 cc/min
Reaction Chamber Pressure	50 mm Hg	200 mm Hg	150 mm Hg	35 mm Hg
Quenching	For H ₂ O: <4% of measured value with gas conditioner For CO ₂ : <1%/vol %CO ₂	Not Reported	Not Reported	Not Reported
Temperature Range	40-104°F	59-95°F	59-95°F	59-95°F

Synthetic Gas Stream

An Environics[®] gas mixing system was used to allow precision blending of the CO₂ with the nitric oxide calibration gases. Figure 2 shows the system used to generate the synthetic gas stream. Mass flow control valves were used to achieve the desired gas concentrations. A computer interfaced to the gas mixing system controlled the mass flow valves, and continuously recorded their positions and flow rates. EPA Protocol 1 NO and CO₂ calibration gases were used in all test runs.

Figure 2
Schematic of the Gas Blending System



DISCUSSION OF TEST RESULTS

Prior to the initiation of any testing, each analyzer was calibrated with span gas (NO in N_2) and zeroed with pure nitrogen. Each potential interferent gas was introduced consecutively along with various NO concentrations. The instrument's response to each of the interferent gases was measured and recorded. The NO_x measurement biases reported represent the difference between the measured concentrations and the input concentrations. Differences in measured NO_x values versus concentration inputs were evaluated for each of the sample conditioning methods under various simulated sample gas conditions.

Eco Physics Model 70E

Four different simulated gas stream blends were tested in the Eco Physics Model 70E NO_x analyzer. One blend was tested at 80 ppmv NO and 15% CO_2 , providing an interference response of -15.13%. For a blend of 25 ppmv NO in 15% CO_2 , the interference response was -13.01%. In the case of 25 ppmv NO in 5% CO_2 blend, the interference bias was reported to be -3.66%. The average CO_2 bias for these three cases was -0.87% per 1% CO_2 in the synthetic gas stream.

In order to evaluate the quenching due to residual water vapor in the sample gas stream, a MAK 6 compressor refrigerant gas conditioner was introduced into the gas sampling system downstream of the gas blending device. The gas exiting the conditioner was maintained at 38°F, and saturated conditions were assumed to exist, giving a water vapor content of approximately 0.8%. A test was performed with 25 ppmv of NO in N_2 with the gas conditioner. An instrument bias of -3.19% was reported. This bias corresponds to a moisture interference response of -3.98% per 1% H_2O in the sample gas. Both the CO_2

and moisture biases are within the manufacturer’s design specification for this instrument. The complete summary of test results for the Eco Physics Model 70E is shown in Table 2.

Table 2
Eco Physics Model 70E Results

Test Condition	CO ₂ in Gas Sample (% vol.)	H ₂ O in Gas Sample (% vol.)	Calibration Gas Value (ppmv)	Instrument Response (ppmv)	Instrument Bias (%)	CO ₂ Bias (%/CO ₂)	Moisture Bias (%/H ₂ O)
NO in N ₂			80.0	80.0			
NO in CO ₂	15.0		80.0	67.9	-15.13	-1.01	
NO in N ₂			25.0	24.6			
NO in CO ₂	15.0		25.0	21.4	-13.01	-0.87	
NO in CO ₂	5.0		25.0	23.7	-3.66	-0.73	
NO in N ₂			25.0	25.1			
NO in N ₂ through MAK Gas Conditioner		0.8	25.0	24.3	-3.19		-3.98

TECO Model 42C

The TECO Model 42C produced quenching bias results similar to the Eco Physics Model 70E although marginally better. The Model 42C was challenged with several different blends of NO in CO₂, and the instrument response was documented. For an input concentration of 15% CO₂ in 80 ppmv of NO, the measurement bias was -14.38%. For an input concentration of 15% CO₂ in 25 ppmv NO, the measurement bias was recorded at -10.8%. For an input concentration of 5% CO₂ in 25 ppmv, the instrument bias was -2.42%. The average CO₂ bias for these three test cases was -0.72% per 1% CO₂ in the synthetic gas stream.

A MAK 6 compressor refrigerant gas conditioner was then introduced into the gas sampling system downstream of the blending device. The gas exiting the conditioner was maintained at 38°F, and saturated conditions were assumed to exist, giving a water vapor content of approximately 0.8%. In an attempt to evaluate the effect of residual water vapor in the gas stream, a test was conducted with 80 ppmv of NO in N₂ diluent gas. An instrument measurement bias of -3.75% was documented. This bias corresponds to a moisture interference response of -4.69% per 1% H₂O in the sample gas. The combined effect of CO₂ and moisture interference was then tested using the MAK gas conditioner in a gas stream containing a blend of 15% CO₂ in 80 ppmv of NO. The instrument measurement bias was documented to be -16.25%.

A second gas conditioner was then tested. A Universal Analyzer Model 3080 thermoelectric gas conditioner was used in place of the MAK 6. The outlet conditions

were maintained as before. A gas sample containing 80 ppmv of NO in N₂ was then introduced to the TECO analyzer. The instrument response was reported to 77 ppmv giving a measurement bias of -3.75%, which was identical to instrument response with the MAK 6 conditioner. A complete summary of all test results is provided in Table 3.

Table 3
TECO Model 42C Results

Test Condition	CO ₂ in Sample Gas (% vol.)	H ₂ O in Sample Gas (% vol.)	Calibration Gas Value (ppmv)	Instrument Response (ppmv)	Instrument Bias (%)	CO ₂ Bias (%/CO ₂)	Moisture Bias (%/H ₂ O)
NO in N ₂			80.0	80.0			
NO in CO ₂	15.0		80.0	68.5	-14.38	-0.96	
NO in N ₂			25.0	24.8			
NO in CO ₂	15.0		25.0	22.3	-10.80	-0.72	
NO in CO ₂	5.0		25.0	24.2	-2.42	-0.48	
NO in N ₂			25.0	25.0			
NO in N ₂ through MAK Gas Conditioner		0.8	25.0	24.0	-4.00		
NO in N ₂			80.0	80.0			
NO in N ₂ through MAK Gas Conditioner		0.8	80.0	77.0	-3.75		-4.69
NO in CO ₂ through MAK Gas Conditioner	15.0	0.8	80.0	67.0	-16.25		
NO in N ₂ through MAK Gas Conditioner		0.8	80.0	77.0	-3.75		-4.69
NO in N ₂ through Universal Gas Conditioner		0.8	80.0	77.0	-3.75		-4.69

TECO Model 42C Low Source

The third analyzer tested was the TECO Model 42C Low Source analyzer. This analyzer was tested with three different concentrations of NO in CO₂ in order to characterize the CO₂ quenching effect. For an input concentration of 15% CO₂ in 80 ppmv of NO, the measurement bias was -9.13%. For an input concentration of 15% CO₂ in 25 ppmv NO, the measurement bias was recorded at -7.09%. For an input concentration of 5% CO₂ in 25 ppmv, the instrument bias was -1.97%. The average CO₂ bias for these three test cases was -0.49% per 1% CO₂ in the synthetic gas stream.

A Universal Analyzer Model 3080 thermoelectric gas conditioner was then introduced into the gas sampling system downstream of the blending device. The gas exiting the

conditioner was maintained at 38°F, and saturated conditions were assumed to exist, giving a water vapor content of approximately 0.8%. A test was conducted with 80 ppmv of NO in N₂ diluent gas. An instrument measurement bias of -0.63% was documented. This bias corresponds to a moisture interference response of -0.78% per 1% H₂O in the sample gas. In order to simulate a wet gas stream, the inlet to the gas passage was wetted with water using a squeeze bottle. The sampling system was continuously run for approximately one hour with the additional water in the gas inlet. The instrument response did not change.

The Universal thermoelectric gas conditioner was then replaced by a MAK 6 compressor refrigerant gas conditioner. The same NO inlet concentration of 80 ppmv was tested. The instrument response bias was -1.25%, which corresponds to a moisture interference response of -1.56% per 1% H₂O in the sample gas.

The TECO Model 42C Low Source analyzer was not as sensitive to CO₂ or moisture quenching as compared to the Eco Physics Model 70E and the TECO Model 42C instruments. The complete test result summary is provided in Table 4.

Table 4
TECO Model 42C (Low Source) Results

Test Condition	CO ₂ in Sample Gas (% vol.)	H ₂ O in Sample Gas (% vol.)	Calibration Gas Value (ppmv)	Instrument Response (ppmv)	Instrument Bias (%)	CO ₂ Bias (%/CO ₂)	Moisture Bias (%/H ₂ O)
NO in N ₂			80.0	80.0			
NO in CO ₂	15.0		80.0	72.7	-9.13	-0.61	
NO in N ₂			25.0	25.4			
NO in CO ₂	15.0		25.0	23.6	-7.09	-0.47	
NO in CO ₂	5.0		25.0	24.9	-1.97	-0.39	
NO in N ₂			25.0	25.6			
NO in N ₂			80.0	80.0			
NO in N ₂ through Universal Gas Conditioner (dry)		0.8	80.0	79.5	-0.63		-0.78
NO in N ₂ through Universal Gas Conditioner (wet)			80.0	79.5	-0.63		-0.78
NO in N ₂ through MAK Gas Conditioner (dry)		0.8	80.0	79.0	-1.25		-1.56
NO in N ₂ through MAK Gas Conditioner (wet)			80.0	79.5	-0.63		-0.78

TECO Model 42CHL

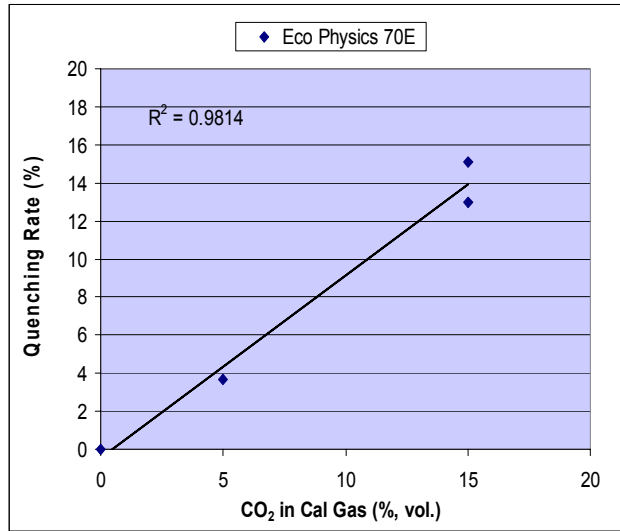
The TECO Model 42CHL NO_x analyzer was the least sensitive to the CO₂ quenching effect of the four analyzers tested. This analyzer was tested with two different blends of NO in CO₂. For an input concentration of 80 ppmv of NO in 15% CO₂, the measurement bias was -5.25%. For the second test case, the input concentration was 25 ppmv of NO in 15% CO₂. The instrument measurement bias was -4.80%. The average CO₂ bias for this analyzer was -0.34% per 1% CO₂ in the synthetic gas stream. Table 5 summarizes the test results for the TECO Model 42CHL analyzer.

Table 5
TECO Model 42CHL Results

Test Condition	CO ₂ in Sample Gas (% vol.)	H ₂ O in Sample Gas (% vol.)	Calibration Gas Value (ppmv)	Instrument Response (ppmv)	Instrument Bias (%)	CO ₂ Bias (%/1% CO ₂)	Moisture Bias (%/1% H ₂ O)
NO in N ₂			80.0	80.0			
NO in CO ₂	15.0		80.0	75.8	-5.25	-0.35	
NO in N ₂			25.0	25.0			
NO in CO ₂	15.0		25.0	23.8	-4.80	-0.32	
NO in N ₂			25.0	25.0			

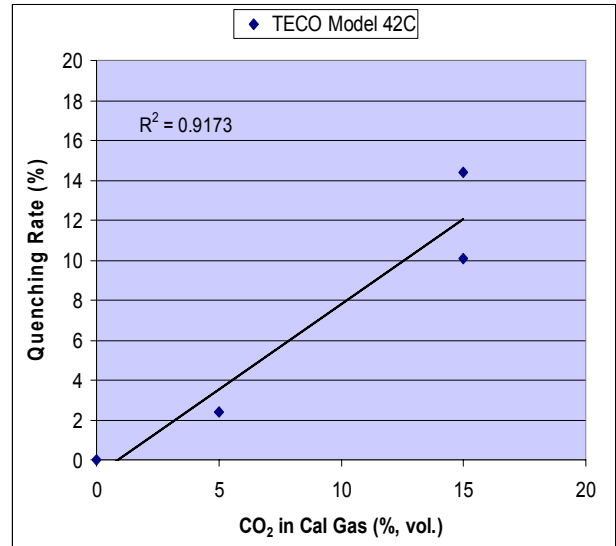
Figures 3 through 6 show the CO₂ quenching rate as a function of CO₂ concentration in the gas stream for the four analyzers tested. As was discussed early, CO₂ quenching had the greatest effect on the Eco Physic Model 70E analyzer performance. Conversely, the operational performance of the TECO Model 42CHL analyzer was least affected by chemiluminescence quenching. The slope of the first order curve fit of the Eco Physics Model 70E analyzer is approximately 2.8 times higher than that of the TECO Model 42CHL analyzer.

Figure 3



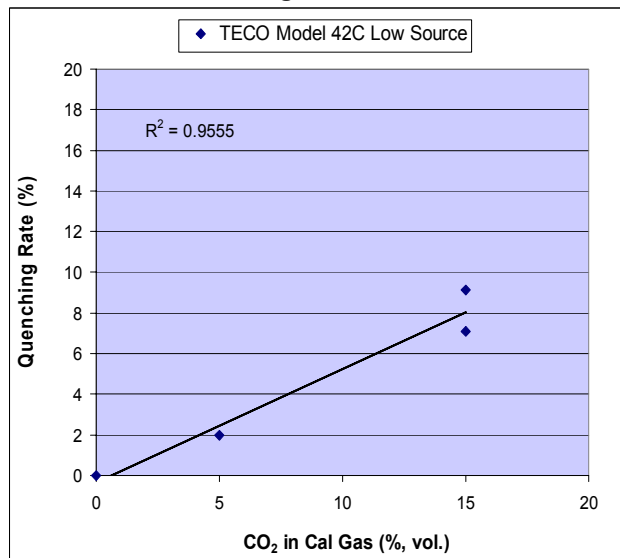
Quenching Rate = 0.96*(% CO₂) - 0.46
 NO_{x,corr} = NO_{x,meas} + ((0.96*(%CO₂) - 0.46)/100)*NO_{x,meas}

Figure 4



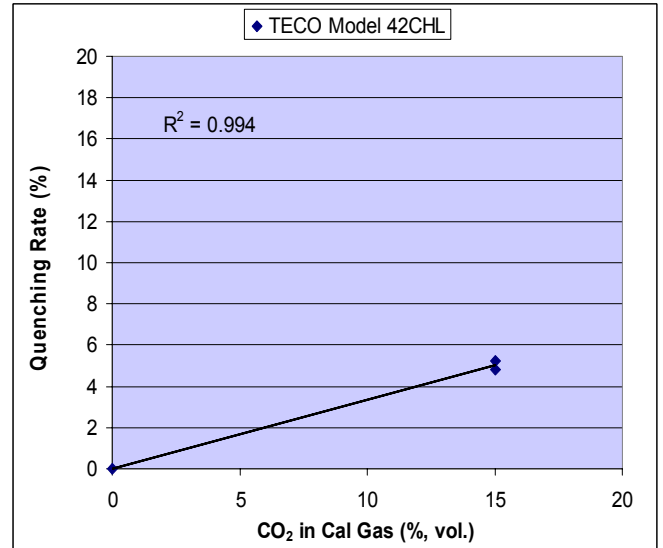
Quenching Rate = 0.85*(%CO₂) - 0.74
 NO_{x,corr} = NO_{x,meas} + ((0.85*(%CO₂) - 0.74)/100)*NO_{x,meas}

Figure 5



Quenching Rate = 0.56*(%CO₂) - 0.33
 NO_{x,corr} = NO_{x,meas} + ((0.56*(%CO₂) - 0.33)/100)*NO_{x,meas}

Figure 6



Quenching Rate = 0.34*(%CO₂)
 NO_{x,corr} = NO_{x,meas} + (0.34*(%CO₂)/100)*NO_{x,meas}

SUMMARY

Four commercially available chemiluminescent NO_x analyzers were evaluated during the course of this investigation. The investigation was designed to examine the quenching phenomena that may interfere with the accurate analysis of nitric oxide with chemiluminescent analyzers. The third body quenching effect was found to be most significant in those gas samples that have large concentrations of CO₂. If this effect is unaccounted for, it may be a significant source of error in the chemiluminescent analysis of combustion gas streams, generally leading to an indicated NO reading that is too low.

The quenching effect is a highly dependent on the type of analyzer used. The worst performing analyzer had an inherent bias that was 2.55 times higher than the best performing analyzer on a percent bias per percent CO₂ basis. The principal reason for this discrepancy is most likely related to the O₃/sample ratio in the reaction chamber. Higher O₃ concentrations in the reaction chamber probably limit the frequency of third body collisions, and at higher pressures, the light energy produced by the chemiluminescent reaction can be absorbed by CO₂ and H₂O.

Ambient and source NO_x analyzers are not inter-changeable. Ambient monitors that traditionally measure NO_x emissions in the ppb range are not necessarily directly applicable to a monitoring situation from a low emission (i.e. less than 10 ppm) combustion source. Ambient gas (air) composition is markedly different than that of a combustion effluent stream. The ambient gas sample is clean, relatively dry at ambient temperatures, and contains very little CO₂ and water.

CONCLUSIONS

1. CO₂ and moisture quenches the chemiluminescence resulting from the reaction between nitric oxide and ozone, causing negative interference. Quenching is a potentially significant source of error in chemiluminescent NO_x analyzers.
2. The degree of this interference varies depending on the pressure and flow rate in the reaction chamber.
3. If there is a great difference between the CO₂ content of the calibration gas and that of the measured gas, the measurement is particularly affected.
4. The bias introduced by gas conditioners as a result of residual moisture in the gas stream is measurable.
5. In order to mitigate the potential for error due to CO₂ in the flue gas, the nitric oxide calibration gas should be a three component blend of NO, CO₂ and N₂. The CO₂ content of the calibration gas should be similar (± 2 mole percent) to the CO₂ content of the sample gas.

6. In the absence of a suitable calibration gas blend, a correction factor should be applied based on test data or vendor supplied data which demonstrates the degree of CO₂ quenching as a relative error per mole percent of CO₂ content.
7. The CO₂ and moisture quenching effects are cumulative.

REFERENCES

1. Matthews, R.D., Sawyer, R.F., and Schefer, R.W. (1977). Interferences in Chemiluminescent Measurement of NO and NO₂ Emissions from Combustion Systems. *Environmental Science & Technology*, Vol. 11: 1092-1096.