

# Chemiluminescence NO<sub>x</sub> and GFC NDIR CO Analyzers For Low Level Source Monitoring

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## ABSTRACT

New combustion sources are experiencing a seemingly never ending lowering of permit limits for NO<sub>x</sub> and CO emissions. The new NO<sub>x</sub> limits are now generally less than 10 ppm. Additionally, many existing sources are being required to control NO<sub>x</sub> emissions to comply with future NO<sub>x</sub> Budget regulations. The new and existing combustion sources require greater measurement precision and accuracy from the NO<sub>x</sub> and CO analyzers installed to continuously monitor the low NO<sub>x</sub> and CO emissions. Additionally, and more critically, greater measurement precision and accuracy is required for the reference NO<sub>x</sub> and CO analyzers used to perform relative accuracy performance testing for the low NO<sub>x</sub> and CO CEMS installed on the low NO<sub>x</sub> and CO emissions sources

Historically, the use of chemiluminescence to detect NO/NO<sub>x</sub> has shown itself to be an excellent gas monitoring method. EPA's NO<sub>x</sub> Reference Test Methods 20 and 7E were based on, and written for, chemiluminescence NO<sub>x</sub> analyzers. The interference (quenching) of gases such as CO<sub>2</sub> with the chemiluminescent process is inherent in all chemiluminescence analyzers; it cannot be eliminated completely, only minimized. A properly optimized chemiluminescence analyzer measuring single digit ppm NO<sub>x</sub> emissions will have minimal and very acceptable interference errors from CO<sub>2</sub> and O<sub>2</sub> background gases. EPA's Reference Test Method 10 for CO monitoring was originally designed for CO monitors to operate in the range of 0 - 1000 ppm, with a minimum detection range of 20 ppm. Contemporary CO limits for gas turbines and other combustion sources are typically below 50 ppm.

This paper will describe in detail how Thermo Environmental Instruments has engineered its new Model 42C-*Low Source* NO<sub>x</sub> analyzer to meet the monitoring needs of the gas-fired turbine industry with single digit ppm NO<sub>x</sub> levels and percent level CO<sub>2</sub> and O<sub>2</sub> diluent gas concentrations

This paper will also describe how Thermo Environmental Instruments has engineered the gas filter correlation (GFC) technique in its Model 48C - CO analyzer to give excellent reliability and good selectivity with high rejection ratio to CO<sub>2</sub> interference for low level CO emissions monitoring.

## INTRODUCTION

New combustion sources are experiencing a seemingly never ending lowering of permit limits for NO<sub>x</sub> and CO emissions. The new NO<sub>x</sub> and CO limits are now generally less than 10 ppm. Additionally, many existing sources are being required to control NO<sub>x</sub> emissions to comply with future NO<sub>x</sub> Budget regulations. The new and existing combustion sources require greater measurement precision and accuracy from the NO<sub>x</sub> and CO analyzers installed to continuously monitor the low NO<sub>x</sub> and CO emissions. Additionally, and more critically, greater measurement precision and accuracy is required for the reference NO<sub>x</sub> and CO analyzers used to perform relative accuracy performance testing for the low NO<sub>x</sub> and CO CEMS installed on the low NO<sub>x</sub> and CO emissions sources

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This paper will describe in detail the operational technique of NO-NO<sub>2</sub>-NO<sub>x</sub> chemiluminescence analyzers. Additionally, this paper will describe how Thermo Environmental Instruments has engineered its new Model 42C-*Low Source* NO<sub>x</sub> analyzer to meet the monitoring needs of the gas-fired turbine industry with single digit ppm NO<sub>x</sub> levels and percent level CO<sub>2</sub> and O<sub>2</sub> diluent gas concentrations.

This paper will also describe in detail the operational technique of the non-dispersive infrared (NDIR) gas filter correlation (GFC) technique for low level CO monitoring. Additionally, this paper will describe how Thermo Environmental Instruments has engineered the NDIR GFC technique in its Model 48C - CO analyzer to give excellent reliability, good selectivity and high rejection ratio to CO<sub>2</sub> interference for low level CO emissions monitoring.

## PRINCIPLES OF OPERATION OF A CHEMILUMINESCENT NO<sub>x</sub> ANALYZER<sup>3,4</sup>

Chemiluminescence, a chemical reaction once dismissed as a laboratory curiosity, has become the most widely used NO<sub>x</sub> emissions monitoring technique in stack emissions and ambient air-monitoring instrumentation. More than 95% of the NO<sub>x</sub> CEMS used by the electric utility industry<sup>1</sup>, and approximately 99% of the NO<sub>x</sub> analyzers used for EPA

Reference Method 7E and 20 testing employ the chemiluminescence measurement technology. The basic chemiluminescence chemistry was delineated in 1967 by Clough et al<sup>2</sup>.

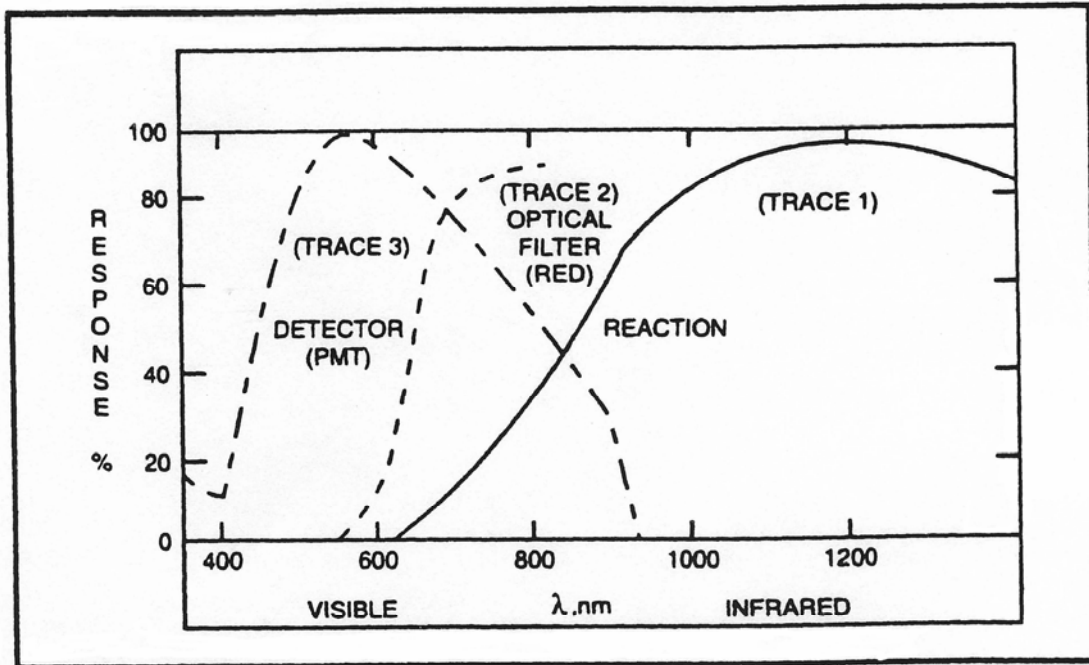


$h\nu$  = photons, M = any compound

Equations 1 and 3 describe the technique employed in commercial instrumentation to measure nitrogen oxides. When NO reacts with O<sub>3</sub>, some electronically-excited NO<sub>2</sub><sup>\*</sup> molecules are produced (Equation 1). These molecules may give off energy in the form of light emission with intensity linearly proportional to the concentration of NO (Equation 3). When the emitted radiation is monitored, it becomes a measure of the concentration of the NO in the reacting sample. The light emission occurs between 600 and 3,000 nm, with a peak at about 1,200 nm. Chemiluminescence NO<sub>x</sub> analyzers measure NO concentrations by using a bandpass filter to select light in the region from about 600 to 900 nm (See Figure 1).

The reactions described by equations 2 and 4 describe a potential limitation to the measurement technique. Only a fraction of the NO reacts to form NO<sub>2</sub><sup>\*</sup> and emits light. Fortunately, the percentage of NO in the reactor that follows the pathway described by equations 1 and 3 is sufficient to ensure a proportionally linear response in a properly designed instrument. By maintaining the O<sub>3</sub> concentration at a large excess to the NO concentration and with a detection system designed for optimum light-collection efficiency, analyzers have been developed with linear dynamic ranges over 10,000 ppm and with detection limits at the parts per trillion level.

Figure 1 – Chemiluminescence Spectral Response Curves



Spectral Response Curves (Kita, D., Chemiluminescence (CHEMIL) Analyzers)

In order to measure  $\text{NO}_2$  using the same basic mechanism outlined by Equations 1 through 4,  $\text{NO}_2$  is first converted to  $\text{NO}$  (i.e.,  $\text{NO}_2$  to  $\text{NO}$  converter), after which the converted molecules react with ozone along with the original  $\text{NO}$  molecules in the sample. This results in a signal that equals the sum of  $\text{NO}$  and  $\text{NO}_2$ . By taking the difference between the converted and non-converted modes, a measure of the  $\text{NO}_2$  concentration is obtained.

The major advantages of chemiluminescence method over other measurement methods for  $\text{NO}_x$  monitoring include:

- Increased sensitivity (detection limit)
- Improved specificity (accuracy)
- Rapid response time (control)
- Linearity over a wide dynamic range (precision)
- Continuous monitoring (control and reporting)
- Simplicity of design (maintenance)

### Basic $\text{NO}$ - $\text{NO}_2$ - $\text{NO}_x$ Chemiluminescence Instrumentation<sup>3,4</sup>

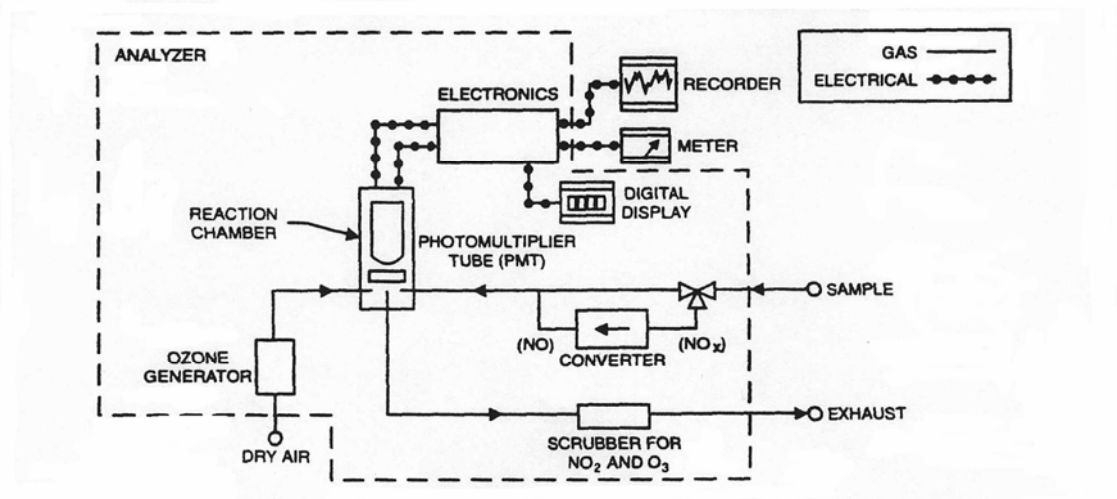
Figure 2 presents a simplified diagram of a  $\text{NO}$ - $\text{NO}_2$ - $\text{NO}_x$  chemiluminescence analyzer as previously described. To measure  $\text{NO}$  concentrations, the sample mixes with ozone in a flow reactor. The ozone required for the reaction is produced within the instrument from dry air or oxygen. The luminescence that results from the reaction of  $\text{NO}$  with  $\text{O}_3$  is monitored through an optical bandpass filter by a high-sensitivity detector positioned at

the end of the reactor. The bandpass filter/detector combination responds to the light emission in a narrow-wavelength band.

Figure 1 shows the spectral output of the chemiluminescence reaction (Trace 1) along with optical filter (Trace 2) and typical detector (photomultiplier tube [PMT]) response (Trace 3) characteristics. As can be seen, only a small portion of the spectrum is monitored. This aids in gaining specificity for the analyzer. An electronic package takes the detector output signal and processes it to voltage, current level, or digital signal.

The sample inlet generally has two flow modes. The first (NO mode) is a direct path of sample to the reaction chamber. Ideally, only the NO in the sample reacts with the ozone to produce light emission (chemiluminescence). In the second mode (NO<sub>x</sub> mode), the sample is routed through a converter that transforms the NO<sub>2</sub> to NO.

**Figure 2 – Basic NO-NO<sub>2</sub>-NO<sub>x</sub> Chemiluminescence Instrumentation**



Basic Chemiluminescence Instrumentation (Kita, D., Chemiluminescence (CHEMIL) Analyzers)

## DESCRIPTION OF A TYPICAL SAMPLE GAS FLOW SYSTEM<sup>3,4</sup>

Figure 2 shows a flow diagram of a typical analyzer. The chemiluminescence method relies on the measurement of the number of NO molecules entering the reaction chamber per time. In order to maintain instrument stability, two gas flow systems are used to regulate a constant flow of ozone and sample gas to the reaction chamber.

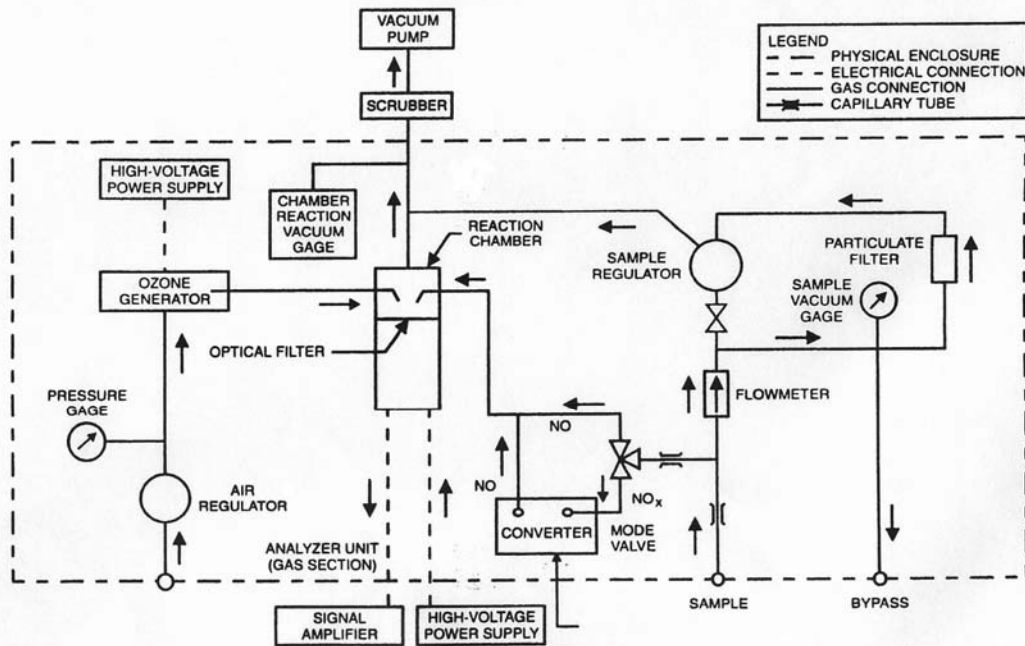
In Figure 3, a single capillary regulates the ozone flow. The function of the capillary is to restrict the flow in the line such that a controllable backpressure is maintained. The pressure upstream of the capillary and the capillary dimensions, and pump characteristics determine the flow. Other flow regulation schemes are possible. Mass flow controller, critical orifices, and the regulation system describe above have been used. All regulation systems are designed for the same purpose: to maintain a constant air or oxygen flow through the ozonator. The prime requirement of the flow system is to maintain a constant

flow of the sample gas to the analyzer as the chemiluminescent reaction is extremely flow sensitive.

Figure 3 presents one standard industrial approach to fulfill these conditions. The total sample passes into the analyzer through the inlet capillary restrictor. A fraction (about 5%) is bled off through a second smaller restrictor and directed to a mode valve. The portion of the sample bypassing the mode valve (and reaction chamber) exits the instrument through a bypass pump. The sample regulator functions to maintain a constant pressure drop across the smaller capillary. This method of flow control maintains a reaction chamber sample flow rate that is insensitive to the sample inlet pressure and total sample flow rate. This type of bypass flow system has the additional advantage of bring the sample to the analyzer. It has the disadvantage of using a fairly large sample flow, which can be a limitation in smog chamber or bag sample studies. For typical process applications, however, there is no sample limitation.

Not all chemiluminescent analyzers use such a bypass-flow technique. Most ambient-air analyzers use only one sample restrictor and no bypass flow. Nevertheless, sample flow remains one of the most critical parameters to control. Mass flow controllers, critical orifices, and/or a regulator and capillary system using a pressure sample have been used.

**Figure 3 – Basic Chemiluminescence Analyzer Flow Diagram**



Basic Chemiluminescence Analyzer Flow Diagram (Kita, D., Chemiluminescence (CHEMIL) Analyzer)

## **Description of Ozone Generation Systems<sup>3,4</sup>**

Although very early prototype analyzers used photolytic sources to generate O<sub>3</sub>, this approach has never been prevalent in commercial instrumentation. The standard approach is the use of the silent-electric or corona discharge. A common design utilizes a condenser-style arrangement with a central electrode, air gap, and outer electrode. Air or oxygen passes over the surfaces of the inner electrode, which is inside a glass envelope, and then passes out to join the sample stream in the reaction chamber. By applying a high alternating or pulsing voltage (about 10,000 VAC) across electrodes, a fraction of the oxygen is broken down into free radicals or single oxygen atoms. The majority of these single atoms combine with O<sub>2</sub> to form ozone (O<sub>3</sub>).

The fraction of ozone produced depends on a variety of different parameters. The level of high voltage, the temperature of the air/oxygen stream, the flow rate through the ozonator, the stability of the voltage source, the gas composition of the ozonator feed, and the physical size of the ozonator all affect the O<sub>3</sub> output. Typical flow rates through commercial ozonators are on the order of 100 cm<sup>3</sup>/min. At this flow rate, with a dry air feed, an ozone percentage of about 0.5% can be achieved. Using oxygen as the ozonator feed, ozone levels of 1 to 2% that can be achieved.

In most cases, where the sensitivity of NO analyzers drops off (becomes sublinear) at high concentrations (>2,000 ppm), the O<sub>3</sub> concentration is no longer in sufficient excess to the NO concentration, making the kinetic assumptions necessary for extended linearity invalid. In order to maintain linearity, it is necessary to increase the O<sub>3</sub> concentration. This is usually done in either of two ways: the sample flow relative to the O<sub>3</sub> flow can be decreased or the O<sub>3</sub> concentration can be increased by using oxygen as the ozonator feed rather than air.

## **DESCRIPTION OF CHEMILUMINESCENCE REACTION CHAMBER<sup>3,4</sup>**

The reaction chamber is a chemically inert enclosed vessel where the ozone and sample streams mix and luminescence is produced. Reaction chambers of polyvinyl chloride, Teflon, aluminum, stainless steel, and gold have been used. The reaction chamber is designed for rapid mixing of the two reagent so that as much of the chemiluminescence occurs in the view of the detector as possible; hence, such factors as operating pressure and gas flow rates will affect the design of the chamber. Usually included as part of the reaction chamber is the optical filter used to block wavelengths not associated with the NO<sub>2</sub><sup>\*</sup> luminescence. Many unsaturated hydrocarbons (e.g., ethylene) and carbonyl compounds (e.g., nickel or iron carbonyl) react with ozone and chemiluminescence. However, the luminescence occurs in the visible or UV regions. By using an appropriate bandpass filter, spectral interference from these types of compounds is virtually eliminated.

## DESCRIPTION OF TYPICAL NO<sub>2</sub> TO NO CONVERTERS<sup>3,4</sup>

The following describes the two types of NO<sub>2</sub> to NO converters primarily used in source and ambient monitoring NO<sub>x</sub> chemiluminescent analyzers. The first converter approach discovered and employed for NO<sub>2</sub> to NO reaction used only heat to drive the reaction. These converters were six feet long, constructed of 316 stainless steel tubing, one-eighth inch in diameter, and heated to between 1200°F and 1470°F (650°C and 800°C). NO<sub>2</sub> passing through this heated tube was reduced to NO for subsequent measurement by the chemiluminescence technique. Converter efficiency (NO<sub>2</sub> to NO conversion) was typically between 97% and 100% and independent of the concentration of NO<sub>x</sub>. Converters of this type (i.e., stainless steel) have been used to monitor NO<sub>x</sub> concentrations from several parts per billion (ppb) to one percent concentrations. This converter relies on the observation that at approximately 1300°F (~700°C) the equilibrium mixture of nitrogen oxides is ~100% shifted to NO. The equation describing this process is:



This converter is still utilized today in virtually all source or high-level nitrogen dioxide measurements.

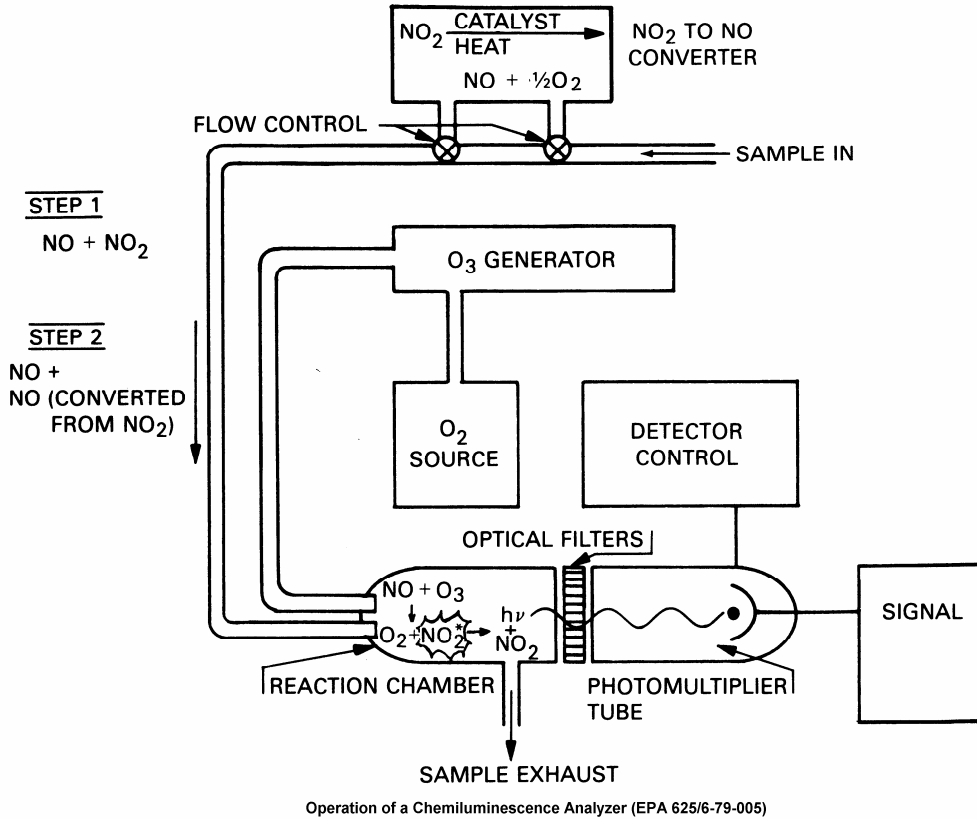
One of the disadvantages of a this approach is that the relatively high temperature required 1200°F (650°C) and 1470°F (800°C) may convert other nitrogen compounds to NO, one particular example being ammonia (NH<sub>3</sub>). This then causes erroneous readings for the NO<sub>2</sub> content of the sample gas.

A second method to reduce NO<sub>2</sub> to NO uses a metal reactant, which is consumed in the process. The most common converter material is molybdenum (Mo). The reaction with molybdenum is as follows:



Since a reactant (e.g. molybdenum) is consumed in this process, these reactors must be removed from service and reconditioned periodically. The advantage of this converter is that it can be operated at lower temperatures, (i.e., 750°F (400°C)), thus reducing the possibility of interference by the conversion of other nitrogen containing compounds to NO. This type of converter has found wide acceptability in instruments designed for ambient air pollution measurements. See Figure 4 for an example of a NO<sub>2</sub> to NO converter in a chemiluminescence monitoring system.

**Figure 4 – Schematic Of A Typical NO<sub>2</sub> – NO Converter System**



## QUENCHING AND VISCOSITY EFFECTS ON NO-NO<sub>2</sub>-NO<sub>x</sub> CHEMILUMINESCENCE MEASUREMENT

The chemiluminescence analyzer is subject to a phenomenon of what is termed quenching. Quenching, simply stated, is a chemical reaction happening at the molecular level, whereby light emission, from the reaction used to detect NO, is reduced by collisions with other gas molecules in the sample. In essence, the “collision” is the statistical probability of the NO<sub>2</sub>\* excited stage not realized in the presence of a certain gas vis-à-vis the absence of that gas. For this discussion we will simply call this the “collision.” That is to say, that the increased presence of a gas such as CO<sub>2</sub> will decrease the sensitivity of the analyzer, due to increased collisions with NO<sub>2</sub>\*. The collisions of CO<sub>2</sub> with NO<sub>2</sub>\* will result in less light emitted than if CO<sub>2</sub> were not present. However, a gas such as N<sub>2</sub>, which has less of a quenching effect, will decrease the sensitivity of the analyzer at a different magnitude. Simply stated, the N<sub>2</sub> and NO<sub>2</sub>\* collision will inhibit the light emission less than CO<sub>2</sub> and NO<sub>2</sub>\*. Therefore, N<sub>2</sub> has less quenching tendencies than CO<sub>2</sub>.

The effects of quenching are endemic with all chemiluminescence reactions. However, varying the sample flow rate can mitigate these effects. The flow rate depends on the viscosity of the gas. The viscosity is the internal friction within a gas, caused by molecular attraction, which makes it resist a tendency to flow. Increasing the flow rate

for high CO<sub>2</sub> content samples will increase the analyzer sensitivity, therefore offsetting the quenching effect. These effects have been known and well documented for some time.

Quenching and viscosity are explained in the kinetic-molecular theory. The kinetic-molecular theory states the following:

1. All gases are composed of large and small molecules.
2. These molecules are in constant, random, motion.
3. In gases at ordinary pressures the molecules are separated by distances that are large relative to their size (total volume of molecules is much less than the total volume occupied by the gas).
4. Collisions between molecules transfer energy without loss.
5. The force of attraction between molecules is negligible in gases at ordinary pressure.
6. The average kinetic energy of gas molecules is proportional to the absolute temperature, and the pressure exerted by gases is accounted for by the large number of collisions per unit time between gas molecules and the walls of the container.

The importance of the kinetic-molecular theory to the chemiluminescence reaction is very important. What is less generally recognized is that the net sample composition dependence of chemiluminescent analyzers, is not only a function of molecular properties, but also of analyzer design parameters such as sample/ozone flow ratio and reaction chamber pressure and design. The viscosity and molecular mass of the gas, capillary/orifice dimensions, pressure gradients both relative and absolute will affect sample flow to the reactor. The interplay between pressure, mass, viscosity and orifice dimensions is involved and is addressed more thoroughly elsewhere<sup>5,6</sup>, but it is by taking advantage of these relationships that an analyzer may be optimized to offset the effects of quenching (non radioactive deactivation).

Currently, the new gas turbines being permitted and installed generally have single digit ppm NO<sub>x</sub> standards. To obtain single digit ppm NO<sub>x</sub> emissions, add on NO<sub>x</sub> controls are necessary. To obtain the additional NO<sub>x</sub> reduction, generally selective catalytic reduction (SCR) systems with ammonia (NH<sub>3</sub>) injection are installed. As previously discussed, some percentage of NH<sub>3</sub> will converter to NO in stainless steel NO<sub>2</sub> to NO converters unless it is scrubbed prior to entering the converter. Additionally, gas turbines have greater percent CO<sub>2</sub> content than other combustion sources. Accordingly, Thermo Environmental Instruments' Model 42CLS was designed to address these monitoring issues as follows.

1. A proprietary internal NH<sub>3</sub> scrubber eliminates the NH<sub>3</sub>
2. A long life stainless converter is used.
3. The ozone rate to sample flow rate is optimized to minimize quenching.

Figure 4 shows the effects the addition of CO<sub>2</sub> has on the measured NO concentration for two instruments: one designed for source applications (Model 42C-LS) and another for

an ambient environment (Model 42C-Ambient). For the test, instruments running simultaneously are calibrated using NO/N<sub>2</sub> balance diluted with dry air to which CO<sub>2</sub> is added. The dilution caused by the addition of CO<sub>2</sub> has been accounted for. Evident in Figure 5 is that the low source instrument shows a slight positive bias with the addition of CO<sub>2</sub> gas, while the instrument optimized for ambient conditions demonstrates a dramatic negative bias for the same sample gas composition. In this example, the low source instrument operates at a lower pressure than the ambient instrument; thus, the collisional deactivation is minimized and the greater flow behavior of the CO<sub>2</sub> gas increases the observed signal. The ambient instrument also experiences greater flow with the addition of CO<sub>2</sub>, but the additional flow does not compensate the enhanced quenching existent at higher pressure.

**Figure 5 - CO<sub>2</sub> Effects On Reported NO Concentration**

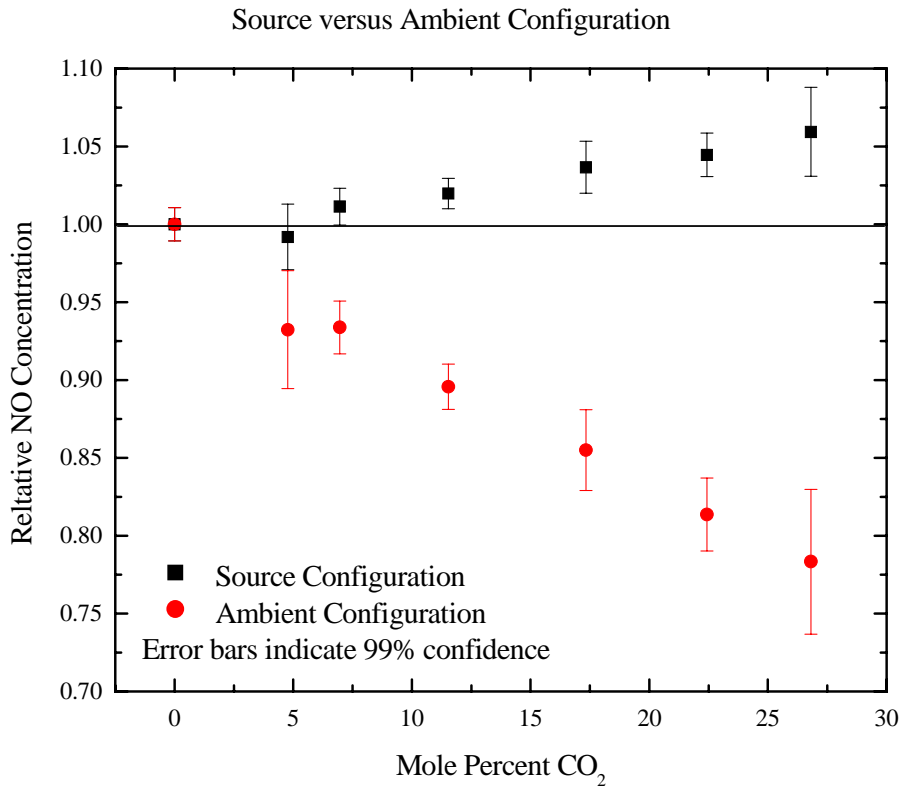


Figure 5 presents the results of two instruments operating side-by-side but optimized for different environments. The two analyzers are fed the same gas. Dry room air is used to feed the ozone generator and the sample gas is drawn from a NO (N<sub>2</sub> balance) calibration gas cylinder diluted with dry air. Additional optimization is possible for the source analyzer for specific source application requirements.

## **ANALYTICAL METHODS FOR MONITORING CARBON MONOXIDE (CO)**

### **Background**

Carbon Monoxide (CO) has a characteristic infrared absorption near 4.6  $\mu\text{m}$ . The absorption of infrared radiation by CO molecules can be used to measure CO concentrations in the presence of other background gases. The non-dispersive infrared (NDIR) technique is based on this principle. The CO NDIR technique is generally accepted as being the most reliable continuous method for measurement of CO in ambient air and also source emissions.

CO gas filter correlation GFC was developed by EPA-sponsored research for low level (ambient) CO measurements more than 20 years ago<sup>7,8</sup>. CO GFC provides good reliability, selectivity and a high rejection ratio to water vapor and CO<sub>2</sub> interference for low level ambient CO emissions monitoring.

### **CO GAS FILTER CORRELATION (GFC) SPECTROMETER PRINCIPLES OF OPERATION 7,8,9**

#### **Basic Components of the Spectrometer**

The technique of GFC spectroscopy offers improved specificity over conventional non-dispersive infrared (NDIR) techniques. GFC spectroscopy is based upon comparison of the detailed structure of the infrared absorption spectrum of the measured gas to that of other gases also present in the sample being analyzed. The technique is implemented by using the measured gas itself, in high concentration, as a filter for the infrared radiation transmitted through the analyzer: hence the term GFC.

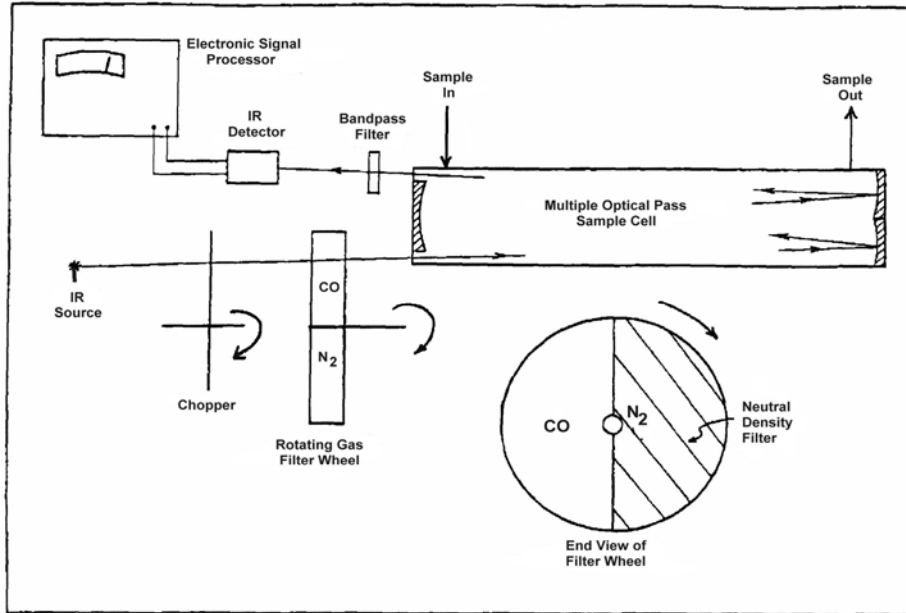
The basic components of a GFC spectrometer for measuring ambient and low source CO are shown in Figure 6. Radiation from an IR source is chopped and then passed through a gas filter, which alternates, between CO and N<sub>2</sub> due to rotation of the filter wheel. The radiation then enters a multiple optical pass sample cell where absorption by the sample gas occurs. The IR radiation exits the sample cell and passes through a narrow bandpass interference filter to fall on an IR detector.

#### **MEASUREMENT OF ZERO GAS**

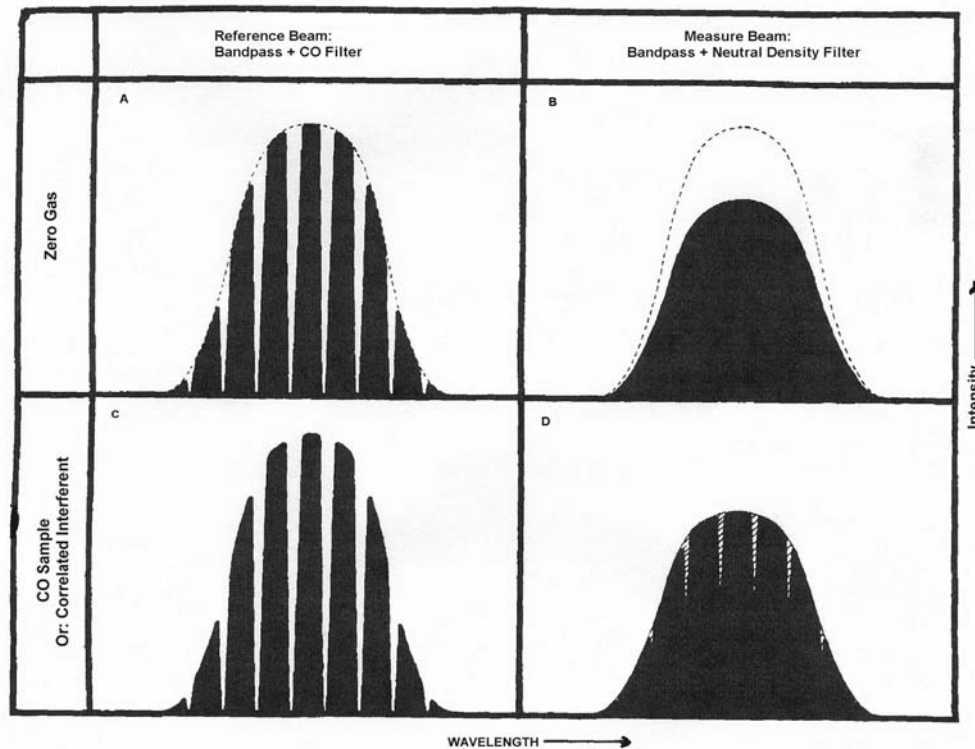
When radiation is passed through the CO filter, and with zero gas (i, e., gas with no infrared absorption) in the sample cell, the spectrum of intensity vs wavelength shown in Figure 7A is received by the detector. The envelope of this curve (dashed line) is due to the narrow bandpass filter, while the gaps are due to the individual lines in the absorption spectrum of CO. The black area is equal to the total energy remaining in the beam. The high concentration ( $\cong 1/2$  atmosphere) of CO in the gas filter has eliminated any radiation,

which can be absorbed by CO; thus, any CO present in the sample cell is unable to further reduce the energy in this beam.

**Figure 6 – Schematic Of A Gas Filter Correlation Spectrometer**



**Figure 7 – Spectra Received By The Detector When Sampling Zero Gas And CO**



However, other gases present in the sample cell, with overlapping but different infrared absorption spectra from that of CO, could absorb energy from this beam. The CO filter, then, acts to produce a reference beam.

When the source energy passes through the N<sub>2</sub> side of the gas filter, there is no absorption by the N<sub>2</sub> and, with zero gas in the sample cell, the dashed curve shown in Figure 7B represents the spectrum, which could fall on the detector. This curve is again due to the bandpass filter. However, an optical balance between this unfiltered beam, and the CO filtered beam, must be obtained. If the gaps shown in Figure 7A were to remove 25% of the area under the dashed curve, then a neutral density filter with 25% attenuation must be placed over the N<sub>2</sub> side of the filter cell to yield a radiation spectrum given by the lower curve in Figure 7B. The attenuator produces a measure beam such that, with zero gas in the sample cell, the solid areas in Figure 7A and 7B (representing the total energies in the reference and measure beams, respectively) are equal. The equal beam energies give a zero difference signal, corresponding to a zero gas sample. Any residual optical imbalance can be cancelled electronically in the signal processor.

## **MEASUREMENT OF CO**

Consider the effect of CO present in the sample cell. The CO cannot absorb radiation from the reference beam, but does from the measure beam, giving rise to the spectra shown in Figure 7C and 7D, respectively. The spectra in Figures 7A and 7C are identical, but the solid area of Figure 7D is reduced from that in Figure 7B by the crosshatched areas, where the CO has absorbed some of the radiation. This difference in energies between the two beams results in an output signal from the analyzer corresponding to the presence of CO in the sample cell.

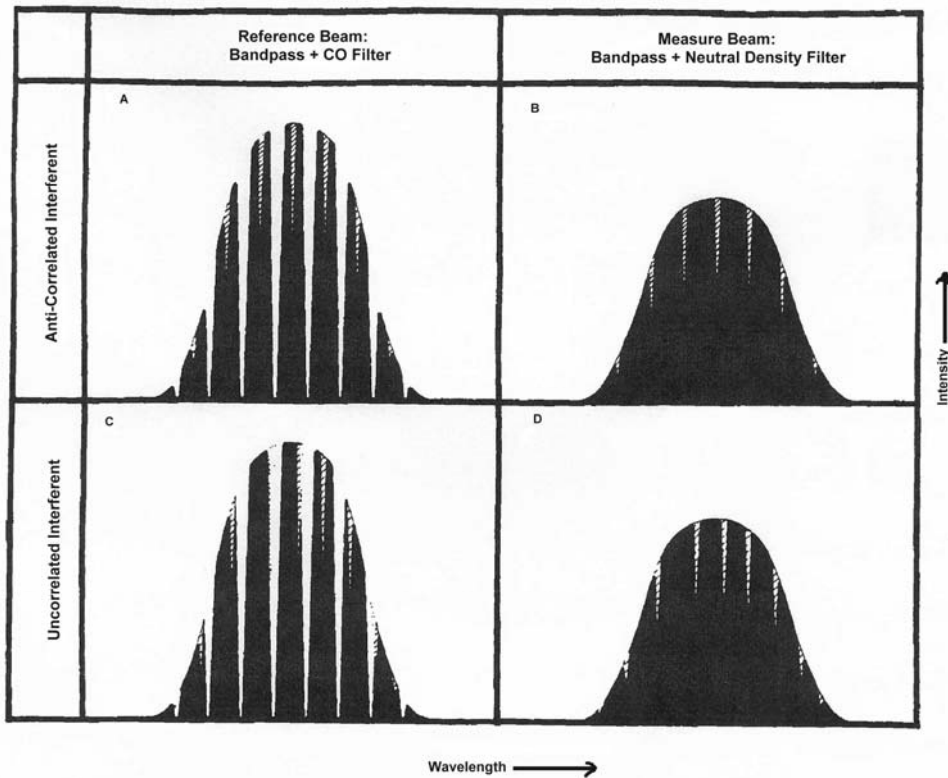
## **DISCRIMINATION AGAINST INTERFERING GASES**

Now consider the effect of an interferent gas, X, present in the sample cell. If all the lines in the absorption spectrum of X occurred at the same wavelengths as those of CO (i.e., perfectly correlated spectra), X would simply mimic CO and give rise to spectra similar to those in Figures 6C and 6D and produce a positive interference.

On the other hand, if the absorption spectrum of X were such that all the absorption lines fell between those of CO (i.e., perfectly anti-correlated spectra), then the spectra shown in Figures 8A and 8B would result. Radiation is now absorbed from the reference beam also. The cross-hatched areas show the energy absorbed from each beam by the interfering gas and the essential feature is that more energy is lost from the reference beam than from the measure beam. This is due to the fact that, in Figure 8A, absorption is occurring from the unattenuated portions of the spectrum, whereas, in Figure 8B, the same degree of absorption is occurring from the lower intensity attenuated spectrum. With CO sample, the measure beam energy is reduced with respect to the reference beam. In this case of a spectrally anti-correlated interfering gas, the reverse is true, i.e., the reference beam energy is reduced with respect to the measure beam, hence a negative interference results.

In practice, spectra are never perfectly correlated or perfectly anti-correlated: indeed, the spectra of unrelated chemical species are uncorrelated.

**Figure 8 – Spectra Received by the Detector when Sampling Interfering Gases**



Figures 8C and 8D show the spectra that might be obtained from a real interfering gas such as water vapor. Each individual line in the absorption spectrum of the interfering gas gives rise to a positive or negative contribution to the total interference according as it is coincident with, or remote from, a CO absorption line. Some lines will be intermediate cases of partial overlap. All three cases are clearly represented in Figure 8C where the dashed lines show where absorption would have occurred if the radiation had not passed through the CO filter.

In the case of totally uncorrelated absorption spectra, the contributions to interference from individual lines cancel each other to produce a net effect of zero interference, or perfect discrimination. In terms of the spectra incident upon the detector in the analyzer, this means that the crosshatched areas in Figures 8C and 8C are equal.

The cross-hatched area in Figure 8A is greater than that in Figure 8B; however, with randomization of the interferent absorption spectrum, some of this area has been lost due to appearance of coincidences with the CO spectrum. The lost areas are shown enclosed by the dashed lines in Figure 8C. For an interferent which is spectrally totally uncorrelated with the measured gas, this reduction of the crosshatched area from the case of Figure 8A to that in Figure 8C is exactly the amount required to equalize the

crosshatched areas of Figures 8C and 8D. This in turn means the solid areas, and hence the beam energies, in Figures 8C and 8D are equal so that no output signal appears from the analyzer, corresponding to perfect discrimination against the interfering gas.

In practice, correlation between spectra is never exactly zero so that a small residual interference could remain; but this is minimized by the bandpass filter which restricts the bandpass of the system to a narrow portion of the spectrum where only the measured gas absorbs strongly.

## **SENSITIVITY**

With the improved rejection of interferences afforded by the GFC technique, it is now feasible to increase the sensitivity of the analyzer. This is achieved in Thermo Environmental Instruments' Model 48C GFC CO analyzer by the multiple pass optics used in the sample cell. The IR beam traverses the cell twenty (20) times, yielding a 20-fold increase in sensitivity over conventional systems using a single pass. This allows full-scale range sensitivity down to 0-1 ppm to be used.

## **CONCLUSIONS**

Today's chemiluminescence NO<sub>x</sub> analyzers and low level GFC NDIR CO analyzers optimized for today's low level (single digit ppm) NO<sub>x</sub> and CO monitoring applications will continue to provide the sensitivity, accuracy and low maintenance historically provided in high level NO<sub>x</sub> and CO continuous monitoring applications.

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## **REFERENCES:**

- 1.) J. Ron Jernigan, P.E., DEE & Charles E. Dene, "Advances in CEMs & Flow Monitoring", Electric Utilities Environmental Conference, Tucson, Arizona, January 1999.
- 2.) Clough, P.N., and Thrush, B.A., "Mechanism of Chemiluminescent Reaction between Nitric Oxide and Ozone," *Transactions of the Faraday Society*, 63, 915-925 (1967)
- 3.) Arvin H. Smith & William J. Zolner, "The Chemiluminescent Analysis of Gaseous Air Pollutants", Thermo Electron Corporation Report – TE305-49-77
- 4.) Dieter Kita, Ph. D., "Chemiluminescence (CHEMIL) Analyzers", Thermo Environmental Instruments

- 5.) Martin F. Zableiski, Daniel J. Seery, Lee G. Dodge, *Environmental Science & Technology.*, 18(2), 1984, 88-92
- 6.) Ronald D. Matthews, Robert F. Sawyer, Robert W. Schefer, *Environmental Science & Technology*, 11(12), 1977, 1092-1096
- 7.) Burch, D.E., Gates, F.J. , Pembroke, J.D., “Ambient CO Monitor”, Final Report on EPA Contract No. 68-02-2219, prepared at Aeronutronic Ford Corp., Newport Beach, Calif., Issued as EPA Report 600/2-76-210, July 1976.
- 8.) Chaney, L.W., Univ. of Michigan and McClenny W.A., EPA, “Unique Ambient Carbon Monoxide Monitor Based on Gas Filter Correlation: Performance and Application”, *Environmental Science & Technology*, Vol. 11, Number 13, December 1977.
- 9.) Appel, Dirk, Thermo Electron Corporation, “Gas Filter Correlation Spectrometer for Ambient CO Monitoring”

## **KEY WORDS**

Low NO<sub>x</sub> monitoring  
Low CO monitoring  
Chemiluminescence NO<sub>x</sub> analyzers  
GFC NDIR CO analyzers