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SENSOR BASED ANALYZER FOR CONTINUOUS EMISSION MONITORING IN GAS PIPELINE APPLICATIONS

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ABSTRACT

Continuous emissions monitoring of gas turbine engines in pipeline service have typically been monitored using either laboratory derived instruments (CEMS) or predicted using data from low cost sensors on the engines and algorithms generated by mapping engine performance (PEMS). A new cost-effective system developed under a program sponsored by the Gas Research Institute (Chicago) combines the advantages of both systems to monitor engine emissions in gas transmission service. This hybrid system is a sensor based analyzer which uses a sensor array, including a newly developed NOx sensor, to directly monitor NOx, CO, and O_2 emissions at the stack. The gases are measured hot and wet.

The new systems were installed and tested on a gas-fired Rolls Royce Spey turbine engine and on Ingersoll-Rand KVG-410 and Cooper GMVH-10 reciprocating engines in gas transmission service. These systems passed the Relative Accuracy Test (Part B) required under U.S. EPA regulations (40 CFR 60).

INTRODUCTION

In the U.S., the Clean Air Act and its Amendments have required installation of continuous emissions monitoring systems (CEMS) for NOx and other combustion products on a wide variety of large emissions sources. These monitoring requirements are just beginning to impact the natural gas pipeline industry through the operating permit programs. Many CEM systems employed in other applications can be adapted for use in the pipeline industry. However, the traditional systems tend to be expensive, and to require significant ongoing maintenance. These needs include the need to operate in unattended facilities, the potential to be mounted in the compressor station's hazardous classified areas (Class 1, Division 1, and Class 1, Division 2 areas), to have a probe that is insensitive to stack vibration, and to provide a wide dynamic range to accommodate the varying engine operating conditions characteristic of pipeline applications. As a result, alternative monitoring methods have been sought to address the cost and maintenance issues, as well as to more effectively meet the needs of gas transmission engines and their compressor stations.

Predictive emission monitoring systems (PEMS) was developed to substitute an array of low cost sensors for the traditional laboratory derived CEM systems. The sensors used vary considerably depending on the predictive system supplier. Installation of a predictive emissions monitoring system has three distinct phases, sensor installation, system mapping, and predictive monitoring. During sensor installation the selected sensors for system monitoring are installed on the engine. On newer engines, many of the required sensors are already present as part of the control system. However, on older engines, new sensors must be installed directly on the engine. After the sensors are installed, mapping begins. During mapping, actual engine emissions and sensor readings are measured instrumentally over a wide range of engine operating conditions. The emissions-sensor reading correlation is then used during normal system operations to predict the actual emissions. Because these systems potentially offer a lower cost alternative to monitoring, while at the same time providing useful information on engine operating conditions, this type of monitoring has been widely tested.

The development of a true NOx sensor allows the user to directly measure NOx like the traditional instrumental approaches, while achieving the potentially lower installed cost from the sensor based predictive monitoring approach. In order to achieve this lower cost, it is necessary to package the array of sensors in a system that does not require the air conditioned shelter traditionally required for CEM systems. Therefore, the system has been designed for direct exposure to the weather for most applications. Where continuous emissions monitoring is required for pipelines, it is typically NOx and oxygen, and sometimes CO which must be monitored. Sensors for each of these gases are in the array. A schematic showing the instrument configuration is shown in Figure 1.

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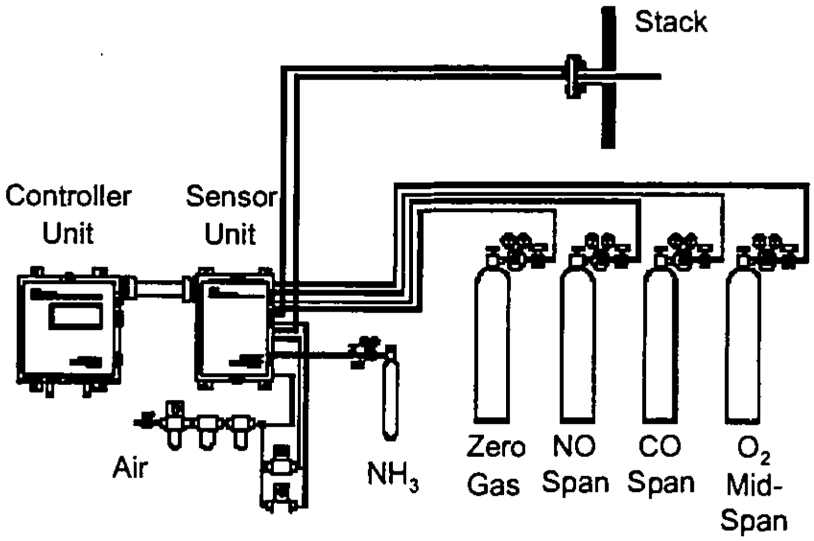

Figure 1. Schematic of the sensor-based analyzer installation on an engine exhaust stack. The CEM unit consists of a sensor units and a controller unit, each housed in a NEMA 4X type box.

Since most U.S. pipelines utilize a considerable variety of engines for transmission, it was desirable to test the effectiveness of the new analyzer on a set of engines which are representative of the range of emissions found in the industry. Three engines were selected: a Rolls Royce Spey gas turbine engine, a Cooper GMVH-10 reciprocating engine; and an Ingersoll-Rand KVG-410 reciprocating engine. Characteristics of these systems are given in Table 1. The typical NOx emissions from these engines vary from a low of about 50 ppm to a high of about 4000 ppm.

Table 1. Characteristics of Engines used in system field tests

Engine Type	Turbine	Reciprocating	Reciprocating
Manufacturer	Rolls Royce	Cooper	Ingersoll-Rand
Model	Spey	GMVH-10	KVG-410
Location	Washington	Louisiana	Texas
Horsepower	16,500	2200	2000
Typical Emissions Ranges			
NOx (ppm)	52-165 ppm	200-300 ppm	2500-4000
CO (ppm)	30-90	50-150	700-6500
O_2 (%)	15-16	14-15	0.2-0.4

In order to confirm the performance of the analyzer, a relative accuracy test was conducted at each of the sites. The tests compared reference method results to the analyzer results. In each case, the analyzer successfully passed the relative accuracy test standards.

SENSOR TECHNOLOGY

The continuous emissions monitor (CEMcat™ analyzer) uses two catalytic sensors, one to measure NOx and one to measure CO. Oxygen is monitored using well-known electro-catalytic zirconium oxide sensor technology. These three sensors are placed within a single heated manifold which contains critical flow orifices to ensure constant flow across each sensor.

The catalytic sensors were both developed specifically for use in combustion systems. Both sensors have the same basic design, but use significantly different catalysts to detect their target gases.

These spark-plug sized sensors have two discrete functional portions: a catalytic sensor element and a reference sensor element (Figure 2). The catalytic element consists of a stainless steel sheath covering a resistive temperature device (RTD). A thin catalytic coating is then applied to the sheath. The catalyst for the CO sensor is a precious metals based material. The NOx sensor uses a vanadium based material (Dalla Betta, 1994). The reference element has the same construction as the catalytic element, but is coated with an inactive ceramic coating.

The catalyst coating is designed to selectively react the gas being measured on its surface, giving off heat (an exothermic reaction). The difference in the resistance of the RTD in the active catalytic element relative to the reference RTD is measured using a bridge circuit. This resistance difference is directly proportional to the concentration of the monitored gas in the total gas stream. Both sensor gives a signal of about 1 Ω at 1000 ppm of the target molecule. A 90% of full scale reading is achieved in 30 seconds.

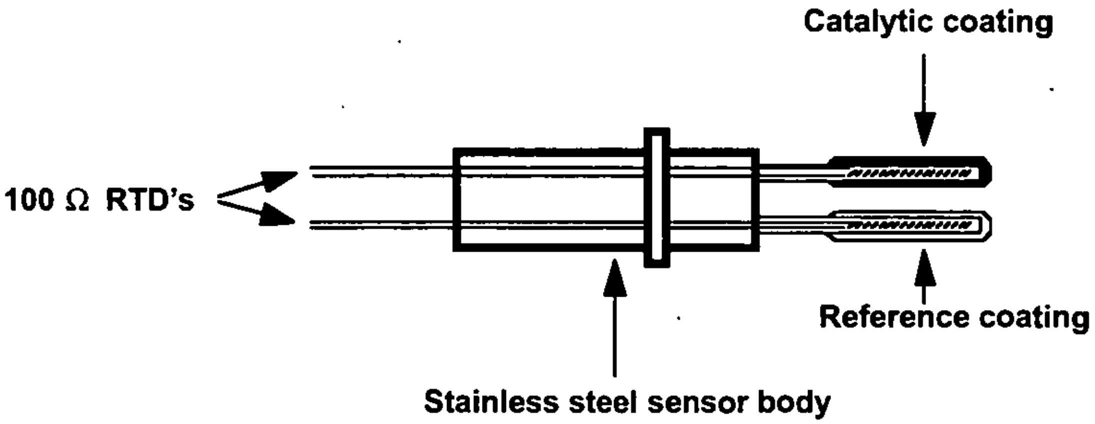

Figure 2. Catalytic sensor schematic. The sensor has two probes, each consisting of a sheathed RTD covered by a coating. One is coated with a catalytic material, and the other with an inactive material. The gas being measured reacts on the active catalyst coating and heat is released. The heat difference between the active and reference probes is used to determine the concentration of the gas of interest in the total gas stream.

In order to ensure that the reaction rate is high, and that condensation does not occur, the sensors are operated at approximately 300 °C (572 °F). The elevated temperature is maintained by housing the sensor in a heated module. The module also serves as a heat exchanger to equilibrate the exhaust gas sample temperature with the sensor temperature. This allows the sensors to give accurate concentrations readings even if there is considerable variation in the engine's exhaust temperature.

The NOx Sensor. The active catalyst on the NOx sensor is a vanadium based catalyst related to the selective catalytic reduction catalysts (SCR) used for catalytic NOx reduction from industrial sources. This catalyst is capable of reducing both NO and NO_2 on its surface in the presence of ammonia as shown in equations (1) and (2).

$$2\,NO + 2\,NH_3 + 1/2\,O_2 \rightarrow 2\,N_2 + 3\,H_2O \qquad \Delta H^\circ_{600\,K} = -97.1\ \text{kcal/mol} \qquad (1)$$

$$2\,NO_2 + 2\,NH_3 \rightarrow 2\,N_2 + 3\,H_2O + 1/2\,O_2 \qquad \Delta H^\circ_{600\,K} = -83.1\ \text{kcal/mol} \qquad (2)$$

For these reactions, trace levels of ammonia are introduced directly into the sensor chamber as a co-reagent. For a source with 50 to 250 ppm of NOx emissions, less than 454 g (1 lb.) of ammonia represent a year's supply. The lack of interfering reactions in the reducing environment of the sensor makes the system highly specific for NOx. Since both NO and NO_2 react on this catalyst, the sensor is a true NOx sensor. Conversion of NO_2 into NO (which is required for chemiluminescence based analyzers) is unnecessary. The NOx sensor shows a linear response to NOx over a very broad range (Figure 3), and can effectively measure NOx between 0 and 10,000 ppm with an accuracy of ± 2 ppm under ideal laboratory conditions.

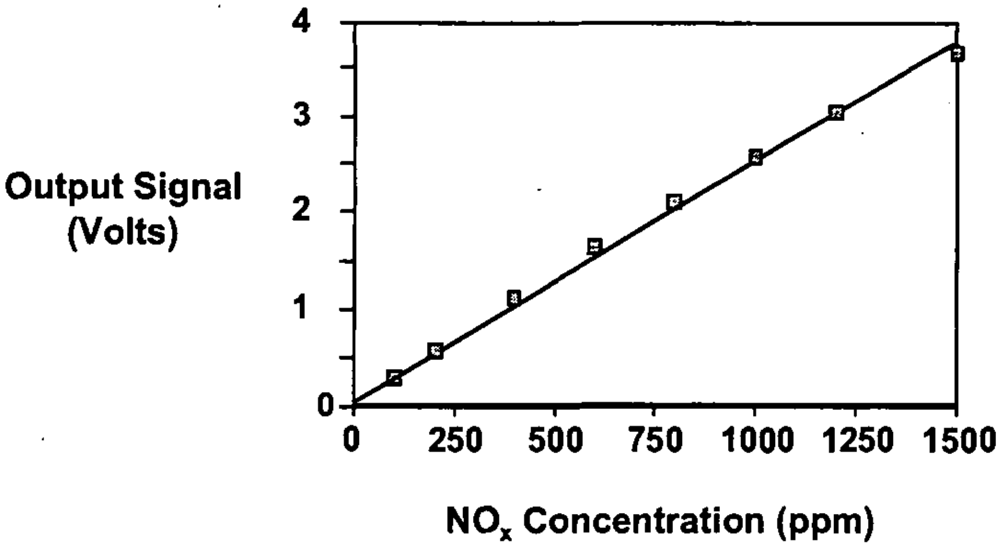

Figure 3. Linearity of the NOx Measurement. The NOx sensor shows excellent linearity over the 0 to 1500 ppm range measured.

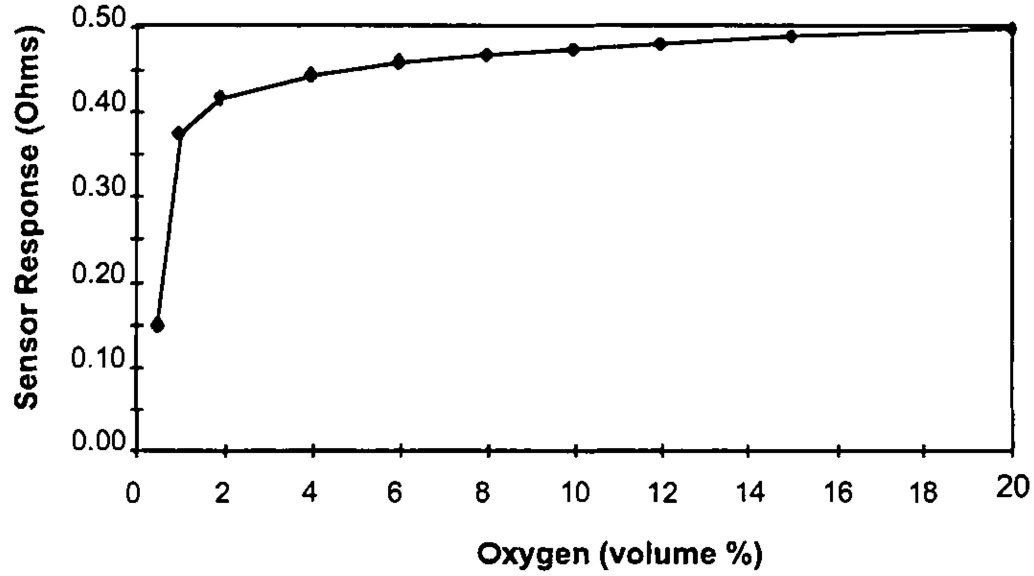

Figure 4. NOx sensor dependency on oxygen concentration. The response of the sensor as a function of oxygen concentration is shown for a sample with 500 ppm NOx at 304 C.

A two fold excess of ammonia is supplied to the sensor to ensure complete reaction and provide a substantial dynamic range during process upsets. Since ammonia also oxidizes over the catalyst, as shown in equation (3), the sensor reading is corrected for the ammonia reaction.

$2\,NH_3 + 3/2\,O_2 \rightarrow N_2 + 3\,H_2O \qquad \Delta H^\circ_{600\,K} = -75.4$ kcal/mol (3)

The NOx sensor response does show a dependency on the oxygen content of the sample stream (Figure 4). In addition, the NOx sensor has a dependency on the water content of the gas stream (Figure 5).

This dependency is not unexpected given the presence of oxygen and water in the NO and NO_2 reductions. The effect is significant primarily at oxygen concentrations below about 5%. The oxygen dependency is corrected using the reading of the oxygen sensor from the sensor array. The water dependency is corrected using actual measured water content, or calculated water content based on fuel flow and excess oxygen levels.

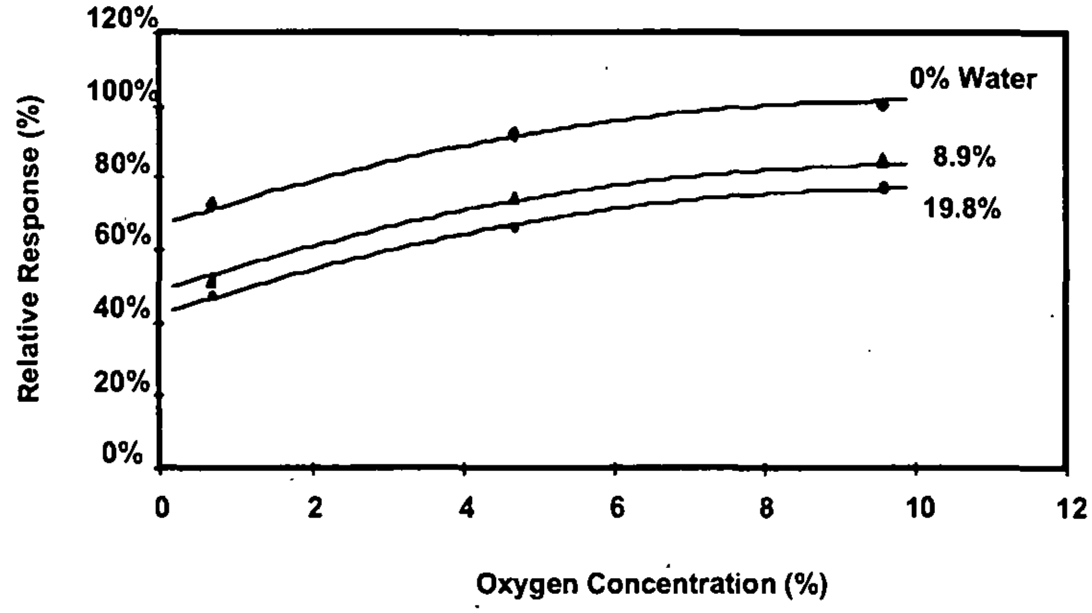

Figure 5. NOx sensor dependency on water and oxygen concentration. The response of the sensor as a function of water and oxygen concentration is shown for a sample with 500 ppm NOx at 304 C.

The CO Sensor. The CO sensor uses a precious metal based catalyst to oxidize CO to CO_2 as shown in equation 4.

$CO + 1/2\, O_2 \rightarrow CO_2$ $\qquad \Delta H^\circ_{800\,K} = -67.6$ kcal/mol (4)

Oxygen present in the exhaust gas serves as the required co-reagent for this oxidation reaction. If there is insufficient oxygen in the exhaust stream, then additional air can be provided to ensure complete reaction.

As with the NOx sensor, the CO sensor has a very broad linear range, and similar accuracy. Figure 6 shows linear performance of the CO sensor from 0 to 1500 ppm of CO, although CO concentrations up to 3 to 5% can be measured using this sensor. This type of catalytic CO sensor has been manufactured by Advanced Sensor Devices (ASD) under the Sonoxco name for about 13 years, and used in large quantities in combustion control applications.

Experience in combustion control applications has shown that these precious metal based sensors also respond to unburned hydrocarbons in the exhaust gases. For example, methane can oxidize over the catalyst as shown in equation (5).

$CH_4 + 2\, O_2 \rightarrow CO_2 + 2\, H_2O$ (5)

However, the catalyst has been optimized to minimize the sensor's response to hydrocarbons. In pipeline applications, methane typically represents more than 90% of the unburned hydrocarbon present in the exhaust stream. Since the CO sensor's response to CO is 150 times greater than its response to methane, there is little effect from these hydrocarbons on the CO measurement. This allows the sensor based continuous emissions monitor to meet regulatory requirements in most applications.

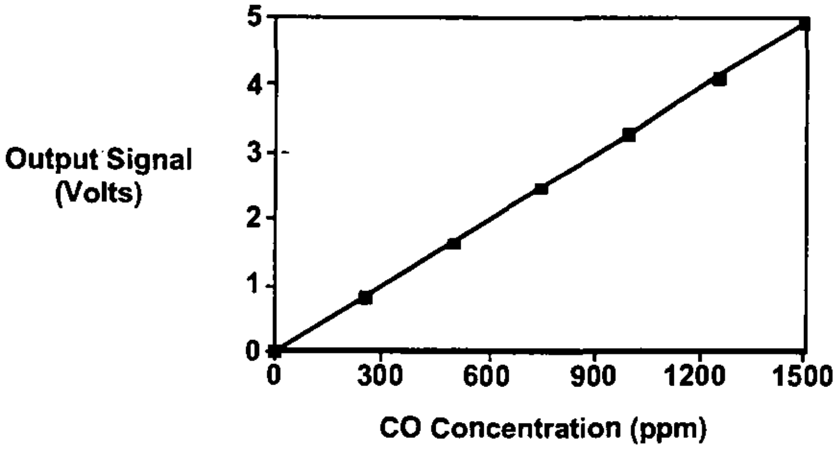

Figure 6. Linearity of the CO Measurement. The CO sensor shows excellent linearity over the 0 to 1500 ppm range measured.

The Oxygen Sensor. The new continuous emissions monitor uses a high performance electrocatalytic zirconium oxide (ZrO_2) based oxygen sensor. These sensors are well characterized, and have been extensively used in emissions monitoring and combustion control applications (Jahnke, 1993). Although the oxygen sensor is housed in the same 300 °C (572 °F) sensor module as the two catalytic sensors, it has its own integral heater which operates at about 850 °C (1550 °F). The high temperature allows the zirconium oxide to operate as a conduit for oxygen between the higher concentration reference side and the lower concentration sample side. The concentration of oxygen is then determined from the electromotive force (emf) produced by this process.

ANALYZER DESIGN

The three sensors have been incorporated into an analyzer designed to take advantage of their performance features. The analyzer consists of two NEMA 4X type enclosures (Figure 1), the controller unit, and the sensor unit. The controller unit contains the system's microprocessor, power supply, I/O modules, analog and digital circuit boards, and keypad/display. The microprocessor converts analog signals from the sensors to a digital form which can be transmitted to the user's data acquisition system using the continuous emissions monitor's RS 485 serial communication port and uses the MODBUS communication protocol. The microprocessor also controls the daily calibration of the unit. The unit can be programmed either using the keypad/display or remotely via the serial port. The microprocessor converts the continuous raw output of the sensor array into compensated one minute average readings for each gas. The regulations require at least one reading per 15 minute period, so this rate is much higher than required.

The sensor unit houses the three sensors, the dual stage air driven aspirator, and the solenoid valves. The dual stage aspirator uses 2 scfm of clean, dry, oil free plant air and draws a sample out of the stack and through the sensor module. Air driven aspirators were selected because they have no moving parts, eliminating maintenance problems frequently encountered with other sample collections systems.

Solenoid valves are the only moving parts in the entire continuous emissions monitor, and are used to introduce the calibration gases for the daily calibration. Since they are located on the clean, dry calibration gases, they are not subject to corrosion and plugging, which is the most frequent failure mode for solenoid valves.

Several different analyzer configurations are possible. The sensor unit can be directly mounted on the exhaust stack, eliminating any need for heated sample lines. The controller unit can then be mounted up to 46 meters (150 feet) from the sensor unit. However, in all three pipeline installations, the controller and sensor units were mounted side by side at ground level, and a short heated sample line (<8 meters, 25 feet) used to take the sample from the exhaust stack mounted probe to the sensor unit. In the turbine application, a Bebco purge system was installed between the two enclosures. This purge system ensured that a positive pressure was maintained in both monitor enclosures, and allowed the entire system to be installed in a Class 1, Division 2 area. The analyzer is designed so that the keypad and readout on the control unit can be accessed without breaking the seal of the unit. The use of the short heated sample line and purge allowed entire unit to be located in a convenient place within the turbine room. The analyzers on the reciprocating engines were not purged. The configurations of each of the systems is given in Teble 2.

Table 2. Installed System Configuration

Engine Type	Turbine	Reciprocating	Reciprocating
Manufacturer	Rolls Royce	Cooper	Ingersoll-Rand
Analyzer Location	Indoor	Outdoor	Outdoor
Purge System	Yes	No	No
Sample Line length (m)	8	6	5

PERFORMANCE TESTING

The objective of the field testing was to demonstrate that the sensor based analyzer was capable of meeting the standards of existing U.S. EPA regulations (US EPA, 1992). This was determined by conducting a Relative Accuracy Test (Appendix B) at each of the field trial sites. These tests were each conducted by third party source testers. In each test the source tester's sample probe was located approximately one foot above the CEMcat analyzer's probe on the engine's exhaust stack. Both probes extended to the approximate center of the stack. The source testers measured NO and NO_2 using reference method 7E. Refarence method 10 was used to monitor CO, and reference method 3A was used for oxygen. Moisture was determined gravimetrically.

The source tester's measurements were compared against the CEMcat analyzer's total NOx, CO, and oxygen obtained from the hot wet exhaust gas. The CEMcat analyzar used calculated water content based on fuel value F factors, and measured oxygen concentrations. NOx and CO were reported and compared in units of ppm, while oxygen and water were reported and compared in units of volume percent.

The relative accuracy test consisted of 9 separate side by side comparisons of the continuous emissions monitoring system against the reference method. Each trial lasted a minimum of 21 minutes. Before and after each trial the source tester re-checked their instrument calibration. The CEMcat system was not adjusted during the test.

The relative accuracy test produces nine separate mean differences (d_i), and one overall average mean difference (d), for each species under comparison. The final calculation of relative accuracy is as follows:

$$\text{Relative Accuracy} = (|d| + |CC|) / \text{Reference Method Mean} * 100 \qquad (4)$$

The value CC, or *confidence coefficient*, is a statistical means to compensate for variations in the data spread between the CEMS and the source tester. Specifically, it is the product of the student t for a 95% confidence interval (t=2.306 for 9 tests), and the standard deviation (*Sd*) of the mean difference between the CEMS and the reference method (d), divided by the square root of the number of trials (n), i.e.

$$CC = (t_{0.95}) \bullet \frac{Sd}{\sqrt{n}} \qquad (5)$$

For the turbine engine and the Cooper reciprocating engine, the engine conditions were kept constant throughout the tests. However, with the Ingersoll-Rand engine the operating conditions were varied, so that each set of three trials was made under a different set of operating conditions. This effectively tested the systems dynamic range and accuracy.

The overall relative accuracies obtained in the test of the turbine and the reciprocating engines are given in Table 3. The U.S. regulations (40 CFR part 60) require a relative accuracy of 20% for NOx, 10% for CO, and either 20% for oxygen or 1% absolute difference for oxygen. The data show that the analyzer is capable of meeting these accuracy requirements.

Table 3. Relative Accuracy Test results under constant engine conditions for the Rolls Royce Spey turbine engine and the Cooper GMVH-10 recirpocating engine.

Engine	Gas	Reference Method (ppm)	CEMcat™ Sensor (ppm)	Difference	Relative Accuracy
Rolls Royce	NOx	110.8 ppm	120.5 ppm	9.7 ppm	11.2%
Turbine CO		60.1 ppm	58.1 ppm	-2.0 ppm	6.7
	O_2	15.6%	14.5%	11.1%	8.9
Cooper	NOx	286.2 ppm	289.3 ppm	3.1 ppm	2.8%
Recip.	CO	80.0 ppm	77.9 ppm	-2.1 ppm	5.0
	O_2	14.6%	14.7%	0.1%	1.6
In-Rand	NOx	2324 ppm	2283 ppm	-41 ppm	0.08%
Recip.	CO	2946 ppm	2982 ppm	36 ppm	4.8
	O_2	0.28%	0.31%	0.03%	

The test with the Ingersoll-Rand engine required the analyzer to measure both NOx and CO over a very wide range of operating conditions. The NOx level varied between approximately 1900 ppm and 2800 ppm while the CO emissions varied between 770 ppm and 5400 ppm. The results of each trial are shown in Figures 7 and 8. The data show that the analyzer met the relative accuracy standards for this engine, and tracked the levels from the source tester over the entire range. Considering that the CO emissions varied by a factor of 8, this represents a significant achievement for the CO sensor.

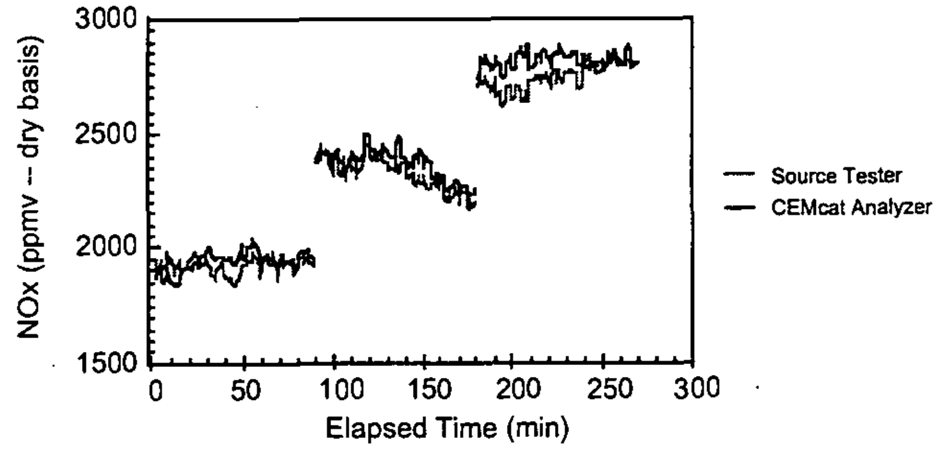

Figure 7. Relative accuracy test results for NOx on Ingersoll-Rand internal combustion engine. The CEMcat™sensor based analyzer results track the source tester over a broad range of concentrations.

CONCLUSIONS

The pipeline industry uses a wide range of engines in its transmission operations. Serving the monitoring needs of this industry with a single type of analyzer requires a system that is capable of effectively monitoring a wide variety of engine types under a wide variety of load conditions. The tests conducted with the sensor based analyzer demonstrate that the system can operate on turbines and reciprocating engines that are representative of the types that are commonly used within the pipeline industry. The tests further demonstrated that even when the engine operating conditions were varied and the emissions levels changed considerably, the sensor based analyzer tracked the engine emissions.

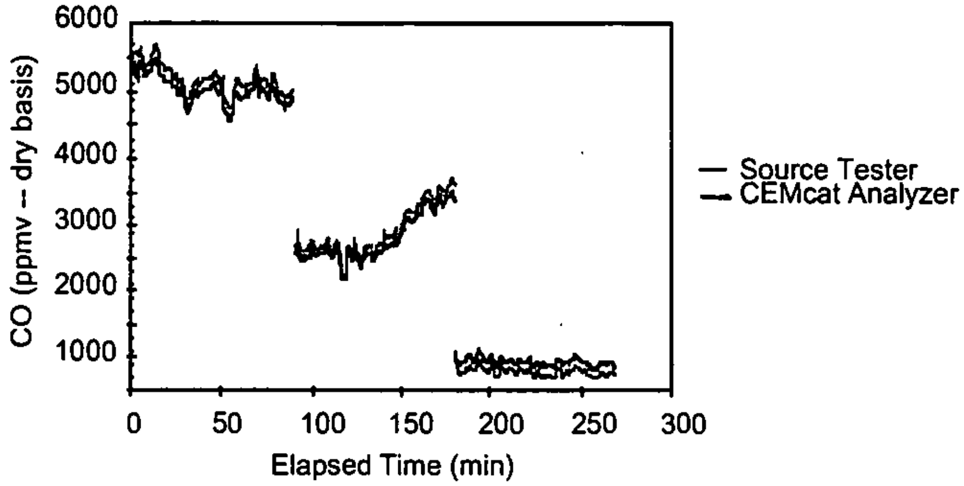

Figure 8. Relative accuracy test results for CO on Ingersoll-Rand internal combustion engine. The CEMcat™sensor based analyzer results track the source tester over a broad range of concentrations.

The ability to track engine emissions with this sensor based analyzer not only means that the system can be used to meet regulatory requirements for emissions monitoring, but it provides potential for control and diagnostic uses. The 4-20 mA output of the monitor could be feed into the station's DCS system, and be used to adjust engine operations to ensure that the system stays below the regulatory limits on emissions. Work on these control applications is just beginning.

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