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NO\(_x\) DESTRUCTION BY CO IN NO\(_x\) TO NO CONVERTERS OF CHEMILUMINESCENT NO ANALYZERS

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An instrument modification for Chemiluminescent NO - NOX Analyzers has been developed which minimizes the NOX destruction in the NOX to NO converters of NO analyzers due to high concentrations of CO. This mechanism causes the NO analyzers to indicate incorrect NOX concentrations when the analyzers are operated in the NOX analysis mode. The modification is applicable to analyzers in which the detection chamber is evacuated.
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INTRODUCTION

The measurement of oxides of nitrogen in a gaseous sample containing significant amounts of carbon monoxide can be highly inaccurate. This report discusses an investigation of this measurement problem and remedial actions taken to minimize this source of error.

Gas analysis of exhaust gases from combustion sources is an important part of many research programs. Of particular interest in many of these programs are the various oxides of nitrogen. The most common instrument for the detection of the oxides of nitrogen is the chemiluminescent analyzer.

The chemiluminescent analyzer offers several advantages which have led to its rapid acceptance. The instrument is specific in its detection of nitric oxide (NO). In addition, the analyzer has a linear response over approximately four decades of NO concentration.

With a suitable converter accessory (which converts the higher oxides of nitrogen into NO) this analyzer can also measure the total oxides of nitrogen (NO\textsubscript{X}). When the converter is utilized, the analyzer indicates the sum of the concentrations of NO and the higher oxides. If one chooses to determine the amount of higher oxides only, then the NO indication must be subtracted from the NO\textsubscript{X} indication.

Many versions of the chemiluminescent analyzer perform the NO detection in an evacuated detector chamber. While a few of the analyzer configurations utilize atmospheric detection, the vacuum detector version offers some distinct advantages. Vacuum detection has an
inherently higher signal to noise ratio. Also, in gas streams with high water content, condensation within the vacuum detector is a lesser problem than in the atmospheric detection method.

At the Lewis Research Center of NASA, the majority of the \( \text{NO-NO}_X \) measurements are being performed with chemiluminescent analyzers with vacuum detection. In the course of gas analysis measurements, a recurring malfunction of the \( \text{NO}_X \) to NO converters has been observed. Since NO is included in any \( \text{NO}_X \) measurement, any \( \text{NO}_X \) measurement should equal or exceed the equivalent NO measurement. However, it has been observed that whenever large amounts of carbon monoxide (CO) are present in the exhaust stream, the indicated \( \text{NO}_X \) measurement is less than the NO indication.

In response to these observations an investigation was conducted to isolate the effect and to determine if modifications could be made to the instrument to circumvent the CO-\( \text{NO}_X \) interaction without causing excessive degradation of the analyzer performance. The results of this investigation are reported herein.

CHEMILUMINESCENT NO-\( \text{NO}_X \) ANALYZERS

The chemiluminescent NO-\( \text{NO}_X \) analyzer is based upon the chemiluminescent reaction of NO with ozone \( (\text{O}_3) \). This reaction has been thoroughly studied and reported (Reference 1) as has the resulting analyzer (References 2 and 3). Thus only a brief description of the analyzer and its components will be presented here.

Figure 1 shows the basic components in a chemiluminescent NO analyzer. A known amount of sample gas is mixed with an excess of \( \text{O}_3 \) in an evacuated reaction chamber. In the resulting reaction, photons of energy are released which are collected and measured by use of a photomultiplier tube. Fixed flow restrictors are utilized to control the flowrates of sample gas and \( \text{O}_3 \). Typical flowrates are 0.05 and 0.12 liter/min. of
sample gas and ozonated air or oxygen ($O_2$), respectively. The conversion of the concept of Figure 1 into a practical, workable instrument requires several steps.

A vacuum pump is necessary, as is a suitable $O_3$ scrubber which will remove any excess $O_3$ from the exhausted gases. The flowrate of sample gas is a critical parameter, so that accurate control of the sample gas inlet pressure is required. Flow control of the $O_3$ is somewhat less critical than that required for the sample gas.

Figure 2 shows the flow pneumatics of a typical commercial NO analyzer with vacuum detection. Of particular interest in Figure 2 is the method of stabilizing the sample gas flowrate into the reaction chamber. A fixed flow restrictor (termed sample restrictor) maintains a constant flowrate from a stable sub-atmospheric pressure level (called sample pressure) into the reaction chamber. The sample pressure is generated by a bypass pump which draws atmospheric air through the sample pressure regulator. This regulator is referenced to the reaction chamber pressure; this is the source of the sample pressure stability.

The sample gas flows into the analyzer through the inlet restrictor. About 5% of this inlet flow is then diverted through the sample restrictor and into the reaction chamber. The remaining sample gas flows through the flow meter, into the regulated sample pressure region, and exits the instrument through the bypass pump. The flowmeter is usually called the "sample flowmeter." In truth, the flow registered is the total sample gas flowrate less that which is diverted into the reaction chamber. The typical sample flowrate is 1 liter/min.

This method of flow control yields a sample gas flowrate into the reaction chamber which is insensitive to the inlet pressure and flow conditions for a wide range of these parameters. This configuration is shared by several of the commercial versions of NO analyzers.

$NO_x$ to NO converters. - The NO analyzer previously described is quite specific in its response to NO with little or no interference from other sample gas constituents. However, in order to broaden the
usefulness of this instrument, a converter accessory is frequently utilized which converts the various oxides of nitrogen (NO\textsubscript{X}) into NO.

Several methods of converting the NO\textsubscript{X} into NO are reported in Reference 4. Probably the most common converter is that which uses heated (650\degree C) stainless steel as the catalyst. The basic configuration of this converter is simply a length of heated small diameter tubing through which the sample gas flows. The stainless steel converter suffers one defect in that it will also convert ammonia into NO.

One manufacturer markets a converter in which the active catalyst is molybdenum. This converter is attractive in that it operates at a much lower temperature (375\degree C). Also, the cooler molybdenum converter will convert only the NO\textsubscript{X} into NO. Reference 5 points out that with both the molybdenum and the stainless steel converters, one may measure NO, NO\textsubscript{X}, and ammonia with a single analyzer.

While it is a common practice to place the converter in the sample gas stream before the analyzer inlet, at least one manufacturer places the converter within the analyzer proper. For clarity, the two locations are termed "upstream" and "internal," respectively. The two locations are shown in Figures 3 and 4.

In Figure 3, for the upstream configuration, the converter is placed in the sample line, along with suitable valving, so that the sample gas flows through the converter (NO\textsubscript{X} mode) or bypasses the converter (NO mode).

In the internal configuration of Figure 4, the converter and valve are moved inside the analyzer and placed between the reaction chamber and the sample capillary. With the internal location, the flowrate through the converter is reduced by a factor of 20:1 over the upstream location. However, the converter operates at or near the reaction chamber pressure of 10 Torr. This makes leak tightness very critical.

Converter efficiency. - Regardless of which converter, or converter location, is used, the efficiency of conversion of NO\textsubscript{X} into NO must be known. No converter is totally efficient in the conversion. Typically, a converter efficiency in excess of 97\% should be expected.
However, converters will and do become less efficient with use. For this reason, it is necessary that the converter be periodically tested to determine its conversion efficiency.

There is a device available, termed a NO\textsubscript{X} generator, which allows converter efficiency to be easily measured. In Reference 6, the specified method for measuring converter efficiency is based upon this device. The methodology of using the NO\textsubscript{X} generator for measuring converter efficiency is well covered in Reference 6.

The converter efficiency is a function of temperature so that the proper operating temperature must be determined and maintained. Due to the nature of the sample gases, fouling of converters does occur so that reactivation and/or cleaning may be periodically required.

Empirically, a purge of the stainless steel converter with air or O\textsubscript{2} is known to be efficacious in maintaining high efficiency. For more severe fouling, a nitric acid wash and distilled water rinse has been successful in recovering lost converter efficiency.

\textbf{CO-NO\textsubscript{X} INTERACTIONS}

In testing combustion sources operating at or beyond stoichiometric conditions, it is not uncommon to observe CO, hydrocarbon and water vapor concentrations greater than 5% each in the exhaust gas stream.

Under the above conditions, malfunctions of the NO analyzers in the NO\textsubscript{X} mode have been observed. In the NO mode, the analyzer performance would be within the bounds of expected results. However, when the converter was valved into the sample gas stream, the NO\textsubscript{X} indication would be markedly less than the NO indication. In addition, the NO\textsubscript{X} indication would continue to decrease with time. Since the NO\textsubscript{X} indication should always equal or exceed the NO indication (NO\textsubscript{X}=NO+higher oxides) it was obvious that a malfunction had occurred.

In the tests described above, if the combustion within the source were readjusted to be below stoichiometric, then the NO\textsubscript{X} indications appeared to recover.
The data and observed effects all indicated that the malfunction mechanism could be localized within the converter. Also, the mechanism involved appeared predominately due to the high CO levels present in the sample gas.

In order to isolate and study these effects, a series of laboratory tests were conducted. The object of the tests was the duplication of the effects in a controlled environment so that various parameters could then be modified, singularly or in combination, at will.

TEST PROCEDURE

All of the tests conducted were performed on chemiluminescent NO analyzers of the vacuum detection type. Four different instruments, from three manufacturers were available for the tests.

Several converters from the three manufacturers were also available; all were stainless steel except for two molybdenum converters. Some converters were new, others were taken from existing analysis systems.

A variety of gases were used, both pure and mixed. Suitable manifolding and flow controllers were utilized so that any or all of the gases could be dynamically blended to controlled concentrations. In addition, a water bubbler was located in the manifold, with valving, so that the gas could be wetted at will. The NO\textsubscript{x} concentrations in the blended gas stream were variable from 50 to 1000 ppm. Figure 5 shows the configuration used in these tests. Figure 5 also lists the gases utilized. All tests used excess blended gas which bypassed the analyzer input and was vented. This method assured uniform inlet pressures.

It is worth noting that accurate knowledge of concentrations was not necessary in this study, since all results were relative. However, it is estimated that the various levels of concentration noted herein were known to ±10% of their true value.
Various combinations of gases were blended and introduced into the flow manifold. Also various analyzers, converters, and converter locations were connected into the manifold while the analyzer output was recorded. When an effect was observed, parameters were manipulated in order to isolate the mechanism involved, and the gases which were active in the effect.

In pursuing the NO\textsubscript{X} destruction mechanism, the exit flow of the converter was passed through CO and carbon dioxide (CO\textsubscript{2}) analyzers. Obviously, this could only be done with the converter operating at atmospheric pressure. This procedure was used to generate the data of Figure 6.

Frequently throughout the test program, converter efficiency was measured using the NO\textsubscript{X} generator method. Also, as required, the converters were reactivated.

As a result of these tests, inferences were drawn concerning the mechanisms involved in the NO\textsubscript{X} to NO converters. All the observations shared one common denominator in that they were qualitative in nature and did not lend themselves to mathematical statement.

RESULTS AND DISCUSSION

CO-NO\textsubscript{X} interactions. - Primary among the effects observed was the anticipated destruction of NO\textsubscript{X} and NO within the converter due to the presence of CO. However, it was observed that the absence of O\textsubscript{2} from the gas was also critical in the CO-NO\textsubscript{X} interaction. In laboratory tests, if the O\textsubscript{2} content of the gas stream was maintained at concentrations of the same order as the CO content, no converter problems were observed.

In combustion exhaust gases, the presence of high concentrations of CO typically implies low O\textsubscript{2} levels. This is exactly the combination of conditions which generate the destruction of NO\textsubscript{X} within the converter. None of the other gases or vapors introduced into the gas
stream appeared to influence the CO-NO\textsubscript{X} interaction. Only O\textsubscript{2}, which inhibited the interaction, showed any measurable influence.

As parameters were varied, concentrations changed, or instruments replaced, one point became evident. Converters and the CO-NO\textsubscript{X} interaction appear to be very sensitive to past events. The manner in which a converter performs is influenced by previous conditions. Also, each converter will behave in a manner unique unto itself.

Figure 6 shows a generalized pattern of converter response which was observed. Bear in mind that all coordinates are very arbitrary. In Figure 6, the input gas stream to the converter was approximately 2\% CO and 100 ppm of NO-NO\textsubscript{X} in N\textsubscript{2}. The first observed change in the gas stream at the converter exit was a net decrease in CO concentration. The amount of loss was very dependent upon flowrate, however, a typical decline would be of the order of 4 to 6\% of the inlet concentration.

The decrease in CO was matched by the appearance of an equivalent amount of CO\textsubscript{2} in the exit flow, even though no CO\textsubscript{2} was present in the inlet flow. The only source of O\textsubscript{2} is the oxide layer on the converter walls.

After a period of time, the CO level would begin to recover, and the CO\textsubscript{2} level would decline. Here, it is assumed that the O\textsubscript{2} source is being depleted. It is at this time that the onset of NO\textsubscript{X} destruction is observed. The elapsed time from the beginning of gas flow until the NO\textsubscript{X} destruction is observed was very sensitive to converter history, gas concentration levels, and the individual converter involved.

If at any time, the CO were removed from the gas stream, the converter exit flow would still show the same NO\textsubscript{X} reduction. Then with time, the NO\textsubscript{X} level would very slowly recover. At any time, the above behavior pattern could be reset to zero time by purging the heated converter with air or O\textsubscript{2}.

The degree of NO\textsubscript{X} destruction observed and discussed above indicated that the oxygen depleted converter was destroying both the higher oxides and NO (NO\textsubscript{X}=NO+higher oxides).

From these observations, it is assumed that the CO-NO\textsubscript{X} interaction is in fact an interaction between CO, NO\textsubscript{X}, and O\textsubscript{2} and that the
interaction occurs on the heated converter wall. Specifically, the following points are predicated as a working hypothesis:

1. Any CO in the gas stream will attack and adsorb oxides from the heated converter wall.
2. Sufficient O\textsubscript{2} will neutralize this oxide loss by acting as a source of replacement O\textsubscript{2}.
3. An oxidized surface within the stainless steel converter is necessary for efficient converter operation.
4. A clean unoxidized converter will destroy NO\textsubscript{X} and NO.

At this point, it should be emphasized that the conventional NO\textsubscript{X} generator test for converter efficiency is not effective in determining efficiency loss due to the above mechanism. The standard method of restoring converter efficiency is a purge with air or O\textsubscript{2}. By design, the gas stream generated by the NO\textsubscript{X} generator has a high O\textsubscript{2} content. Therefore, in the measurement of efficiency, the generator is also reactivating the converter.

**Converter location and type.** - In the previous discussion, the primary variables were gas specie and concentration. These tests were repeated for both converter locations (internal and upstream) and both converter types (stainless steel and molybdenum). The construction of the molybdenum converter was such that it could only be used in the internal location.

With an upstream stainless steel converter, the converter showed apparent efficiency loss in 1 hour with CO levels of 1000 ppm. Probably, by waiting longer, the loss of efficiency could have been observed with lower CO levels. However, in most installations, a converter air purge is utilized when the NO analyzer is in the NO mode of operation. Rarely would any test cycle require NO\textsubscript{X} observations for a time period in excess of 1 hour. Therefore, 1 hour was chosen as a time criteria for observable effects.

When the stainless steel converter was relocated internal to the analyzer, the same effects were not observed until the CO content of the gas stream exceeded about 2\%. This is a 20:1 increase in CO tolerance.
and corresponds to the 20:1 reduction in gas flowrate through the converter in the internal location.

For the molybdenum converter in the internal location, onset of the NO\textsubscript{X} destruction was not observed until the CO concentration exceeded 7%. Here, as with the stainless steel converters, O\textsubscript{2} in the gas stream negated the CO-NO\textsubscript{X} interaction.

**NO ANALYZER MODIFICATION**

The primary object of this study was to circumvent the NO\textsubscript{X} destruction mechanism described above. The first, and obvious step is to use only the internal location for the NO\textsubscript{X} to NO converter. Commercial analyzers are available which utilize the internal location for the converter. Also, existing equipment, with the externally located converter, can be modified and fitted with an internally located converter. Several analyzers from various manufacturers have been modified to accept the internal location of the converter; the required modifications have been minor and easily performed.

The second step in reducing the NO\textsubscript{X} destruction process would be the use of molybdenum converters. With the molybdenum converter, located internally, an analyzer should function properly with CO levels of 7% or less.

An additional action would be the addition of O\textsubscript{2} or air to the sample gas to insure an O\textsubscript{2} concentration of at least 5% in the gas stream passing through the converter. For the upstream converter location, additional measurements of the degree of dilution would be required so that the analyzer indication could be corrected to reflect the NO-NO\textsubscript{X} levels before dilution.

The internal converter location offers an unique opportunity to induce an air purge through the converter which will provide the O\textsubscript{2} dilution and yet require no correction to the data for the dilution. For this type analyzer, if the sample flowrate into the reaction chamber remains
fixed, the analyzer response is relatively unaffected. The chemiluminescent analyzer responds to the number of NO molecules passing through the detector so that sample flowrate is the critical parameter. Pressure within the detector is a secondary factor in that increasing pressure will degrade the analyzer response. Sample flowrate is controlled by the sample capillary; the converter is located between the capillary and the reaction chamber. Low flowrates of O₂ or air can be introduced between the converter and the capillary without changing the sample gas flow and yet provide sufficient O₂ dilution of the sample flowing through the converter.

Figure 7 shows the modification made to introduce air into the internal converter. An additional capillary is installed which provides an air flow of about 0.015 liter/min. into the converter. In practice, the additional flow causes the reaction chamber pressure to increase by about 10%. The air leak was installed such that the leak is continuous, and the sample flowrate is constant in both analyzer modes.

This modification does cause a decrease in analyzer sensitivity due to the increase in the detector chamber pressure. In Figure 8, the effect of reaction chamber pressure upon sensitivity is given. The response curve is quite steep in the vicinity to the 10 Torr operating point of the analyzer. The small increase in reactor chamber pressure has a sizable effect upon analyzer sensitivity. Typically, a net decrease in analyzer sensitivity of about 10\% can be expected. However, the latitude of sensitivity adjustment in most NO analyzers is more than sufficient to compensate for the effect of the air purge.

Using the molybdenum converter in the internal location with an air purge of 15 cc/min., an analyzer was operated successfully in the laboratory with CO and NOₓ in N₂ mixtures (containing no O₂) in which the CO concentration exceeded 30\%.

One of the analyzers, in which the NOₓ destruction effect was first noted, was modified for an internally mounted molybdenum converter with air purge. This analyzer has been in operation for approximately 4 months with no observable degradation of performance or accuracy.
OTHER EFFECTS

An assortment of other effects were observed and deserve reporting.

**NO\textsubscript{X}** absorption in water. - During various test cycles, the gas stream was wetted using a water bubbler. A net loss of NO\textsubscript{X} was observed using the bubbler, and was accompanied by an indicated increase in the acidity of the water.

The solubility of nitrogen dioxide (NO\textsubscript{2}) in water is known, and in designing the sample handling systems of gas analysis instruments, it is routinely assumed that condensate will adsorb a portion of the NO\textsubscript{X} from the sample gas. Here, this loss was demonstrated, proving the validity of the assumption.

The solution to this loss mechanism is straightforward: maintain the gas at a temperature sufficient to prevent condensation. The evacuated reaction chamber of this type of NO analyzer is inherently free of condensation. However, condensation can occur at the analyzer inlet if the analyzer is not equipped with a heated inlet assembly.

Chemiluminescence of hydrocarbons. - During these tests, a response to ethylene (C\textsubscript{2}H\textsubscript{4}) was observed in the NO analyzers. Typically, the magnitude of the C\textsubscript{2}H\textsubscript{4} response was the order of 1/3000 of the equivalent NO response. This means that the analyzer's response to a 1% C\textsubscript{2}H\textsubscript{4} concentration would be equivalent to about 3 ppm NO, indicated. When the C\textsubscript{2}H\textsubscript{4} gas mixture was passed through the stainless steel converter, the analyzer output would drop to about 1/3 of its former level. The implication here is that the C\textsubscript{2}H\textsubscript{4} suffered some destruction within the hot converter environment.

The analyzers showed no response to propane (C\textsubscript{3}H\textsubscript{8}) until the gas was passed through the stainless steel converter. In the NO\textsubscript{X} mode, the analyzers would indicate a slight, but definite, positive interference due to C\textsubscript{3}H\textsubscript{8}. Here, the hypothesis is a cracking of heavier hydrocarbons in the converter, and the generation of a specie (such as C\textsubscript{2}H\textsubscript{4}) which will exhibit chemiluminescence.
When using the lower temperature molybdenum converter, no differences in the analyzer's hydrocarbon response was noted between the NO and NO\textsubscript{X} modes of operation. Apparently, the molybdenum converter environment, operating at a lower temperature, does not react with the hydrocarbons.

The hydrocarbon interferences, although positive, were all of low order. For most applications, the effect is not significant. In those few cases where the effect must be considered, a method for preventing the interferences is not at hand. No solution is offered beyond awareness and tolerance.

**SUMMARY OF RESULTS**

A mechanism of NO\textsubscript{X} destruction, which had been observed in chemiluminescent NO analyzers, was duplicated in the laboratory. The mechanism was identified as an interaction within the NO\textsubscript{X} to NO converter between CO and NO\textsubscript{X}. Appreciable amounts of O\textsubscript{2} (5\% or more) in the gas mixture tended to quench the CO-NO\textsubscript{X} interaction.

A molybdenum converter, mounted in the internal location was found to have the best tolerance to CO in the sample gas. Further, a simple method of adding O\textsubscript{2} to the sample gas via an air purge modification was developed. A chemiluminescent NO analyzer equipped with an internally mounted molybdenum converter and the air purge showed no NO\textsubscript{X} destruction in a sample gas containing 30\% CO and no O\textsubscript{2}.

Other minor effects were noted during the course of this work. The absorption of NO\textsubscript{X} by condensate was observed; this can be prevented by eliminating condensation of water from the sample gas. Also, some positive interferences due to chemiluminescent hydrocarbons were observed. However, apparent cracking of the hydrocarbons within the heated converter appeared to modify the amount of interference.
For the hydrocarbon effects, no specific action to correct the errors are available. Probably in most cases, the effects would be minor. However, the presence of measurement errors due to hydrocarbons must be recognized.

The above effects have been observed with analyzers with vacuum detection. Little or no experience with other analyzer types is available at this laboratory. The suggested solutions to the various problems are in turn specifically directed toward the analyzers with evacuated reaction chambers.

REFERENCES


FIGURE 1. Chemiluminescent NO Analyzer: Conceptual Schematic.
FIGURE 2. Chemiluminescent NO analyzer; typical pneumatics for an analyzer of the vacuum detection type.
FIGURE 3. Typical connection of NO\textsubscript{X} to NO converter for upstream converter configuration.
FIGURE 4. Typical connection of NO\textsubscript{x} to NO converter for internal converter configuration.
Figure 5. Apparatus configuration for CO-NOx interaction tests.
FIGURE 6. Typical observed gas concentrations at the exit of the NOX to NO converter for an input gas flow of CO and NOX in N2.
FIGURE 7. Modification of the NO-NO\textsubscript{X} analyzer (internal converter) for converter air surge.
Figure 8. Chemiluminescent NO Analyzer Response as a Function of Reaction Chamber Pressure. Data taken from Reference 5.