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NO$_X$ DESTRUCTION BY CO IN NO$_X$ TO NO CONVERTERS

OF CHEMILUMINESCENT NO ANALYZERS

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16. Abstract

An instrument modification for Chemiluminescent NO - NO_X Analyzers has been developed which minimizes the NO_X destruction in the NO_X to NO converters of NO analyzers due to high concentrations of CO. This mechanism causes the NO analyzers to indicate incorrect NO_X concentrations when the analyzers are operated in the NO_X 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 contain-
ing 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 im-
portant 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 chemilumi-
nescent analyzer.

The chemiluminescent analyzer offers several advantages which
have led to its rapid acceptance. The instrument is specific in its de-
tection of nitric oxide (NO). In addition, the analyzer has a linear re-
sponse 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_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_X indication.

Many versions of the chemiluminescent analyzer perform the NO
detection in an evacuated detector chamber. While a few of the ana-
lyzer 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 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 NO_X to NO converters has been observed. Since NO is included in any NO_X measurement, any 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 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-NO_X interaction without causing excessive degradation of the analyzer performance. The results of this investigation are reported herein.

CHEMILUMINESCENT NO-NO_X ANALYZERS

The chemiluminescent NO-NO_X analyzer is based upon the chemiluminescent reaction of NO with ozone (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 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 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 exausted 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 reponse 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_x) into NO.

Several methods of converting the NO_x into NO are reported in Reference 4. Probably the most common converter is that which uses heated (650° 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° C). Also, the cooler molybdenum converter will convert only the NO_x into NO. Reference 5 points out that with both the molybdenum and the stainless steel converters, one may measure NO, NO_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_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_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 be .e 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_x generator, which allows converter efficiency to be easily measured. In Reference 6, the spec' fied method for measuring converter efficiency is based upon this devi .e. The methodology of using the NO_x generator for measuring converte. 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_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.

CO-NO_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_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_x indication would be markedly less than the NO indication. In addition, the NO_x indication would continue to decrease with time. Since the NO_x indication should always equal or exceed the NO indication (NO_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_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_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 $\pm 10\%$ 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_x destruction mechanism, the exit flow of the converter was passed through CO and carbon dioxide (CO_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_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_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_x interactions. - Primary among the effects observed was the anticipated destruction of NO_x and NO within the converter due to the presence of CO. However, it was observed that the absence of O_2 from the gas was also critical in the CO-NO_x interaction. In laboratory tests, if the O_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_2 levels. This is exactly the combination of conditions which generate the destruction of NO_x within the converter. None of the other gases or vapors introduced into the gas

stream appeared to influence the $CO-NO_x$ interaction. Only O_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 $CO-NO_x$ 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 $NO-NO_x$ in N_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_2 in the exit flow, even though no CO_2 was present in the inlet flow. The only source of O_2 is the oxide layer on the converter walls.

After a period of time, the CO level would begin to recover, and the CO_2 level would decline. Here, it is assumed that the O_2 source is being depleted. It is at this time that the onset of NO_x destruction is observed. The elapsed time from the beginning of gas flow until the NO_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_x reduction. Then with time, the NO_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_2.

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

From these observations, it is assumed that the $CO-NO_x$ interaction is in fact an interaction between CO, NO_x, and O_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_2 will neutralize this oxide loss by acting as a source of replacement O_2

(3) An oxidized surface within the stainless steel converter is necessary for efficient converter operation.

(4) A clean unoxidized converter will destroy NO_x and NO.

At this point, it should be emphasized that the conventional NO_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_2. By design, the gas stream generated by the NO_x generator has a high O_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_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_x destruction was not observed until the CO concentration exceeded 7%. Here, as with the stainless steel converters, O_2 in the gas stream negated the CO-NO_x interaction.

NO ANALYZER MODIFICATION

The primary object of this study was to circumvent the NO_x destruction mechanism described above. The first, and obvious step is to use only the internal location for the NO_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_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_2 or air to the sample gas to insure an O_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_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_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 uneffected. The chemilumi-
nescent 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 O_2 or air
can be introduced between the converter and the capillary without
changing the sample gas flow and yet provide sufficient O_2 dilution of
the sample flowing through the converter.

Figure 7 shows the modification made to introduce air into the in-
ternal 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 1C . The air leak was installed such that the leak is contin-
uous, 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 oper-
ating 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 NO_x in N_2 mixtures (containing no O_2)
in which the CO concentration exceeded 30%.

One of the analyzers, in which the NO_x destruction effect was
first noted, was modified for an internally mounted molybdenum con-
verter with air purge. This analyzer has been in operation for approx-
imately 4 months with no observable degradation of performance or
accuracy.

OTHER EFFECTS

An assortment of other effects were observed and deserve reporting.

NO_X absorption in water. - During various test cycles, the gas stream was wetted using a water bubbler. A net loss of NO_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_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_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 thest tests, a response to ethylene (C_2H_4) was observed in the NO analyzers. Typically, the magnitude of the C_2H_4 response was the order of 1/3000 of the equivalent NO response. This means that the analyzer's response to a 1% C_2H_4 concentration would be equivalent to about 3 ppm NO, indicated. When the C_2H_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_2H_4 suffered some destruction within the hot converter environment.

The analyzers showed no response to propane (C_3H_8) until the gas was passed through the stainless steel converter. In the NO_X mode, the analyzers would indicate a slight, but definite, positive interference due to C_3H_8. Here, the hypothesis is a cracking of heavier hydrocarbons in the converter, and the generation of a specie (such as C_2H_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_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_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_X to NO converter between CO and NO_X. Appreciable amounts of O_2 (5% or more) in the gas mixture tended to quench the CO-NO_X interaction.

A molybdenum converter, mounted in the internal location was found to have the highest tolerance to CO in the sample gas. Further, a simple method of adding O_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_X destruction in a sample gas containing 30% CO and no O_2.

Other minor effects were noted during the course of this work. The absorption of NO_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.

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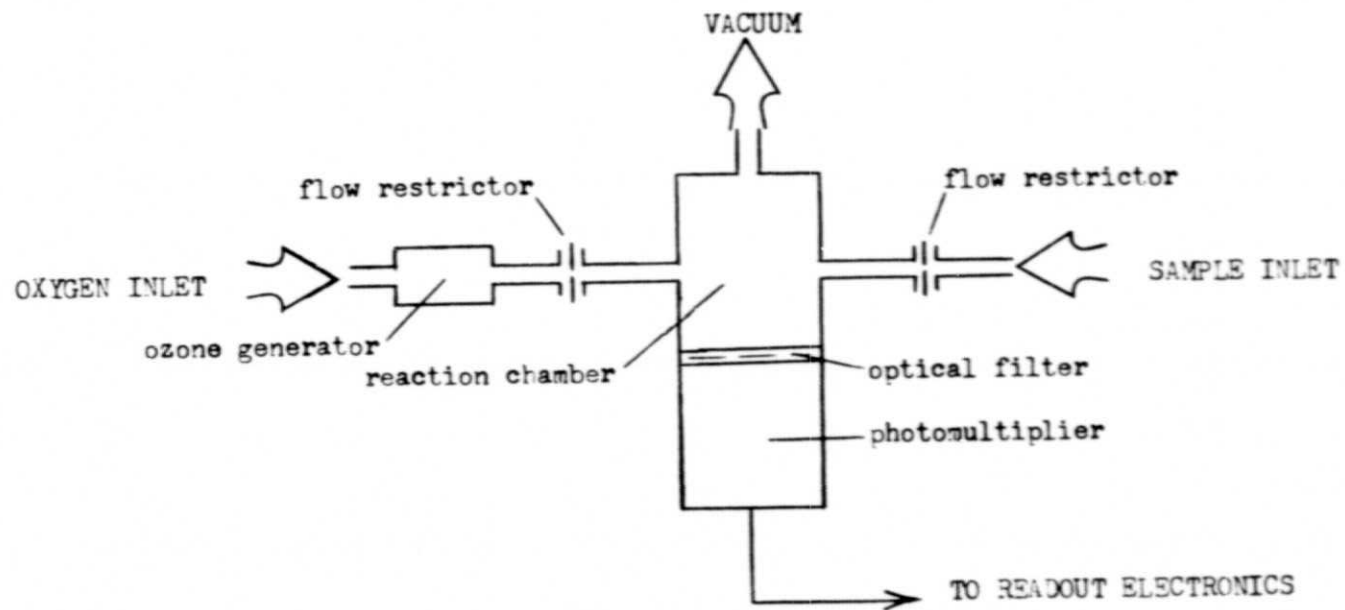
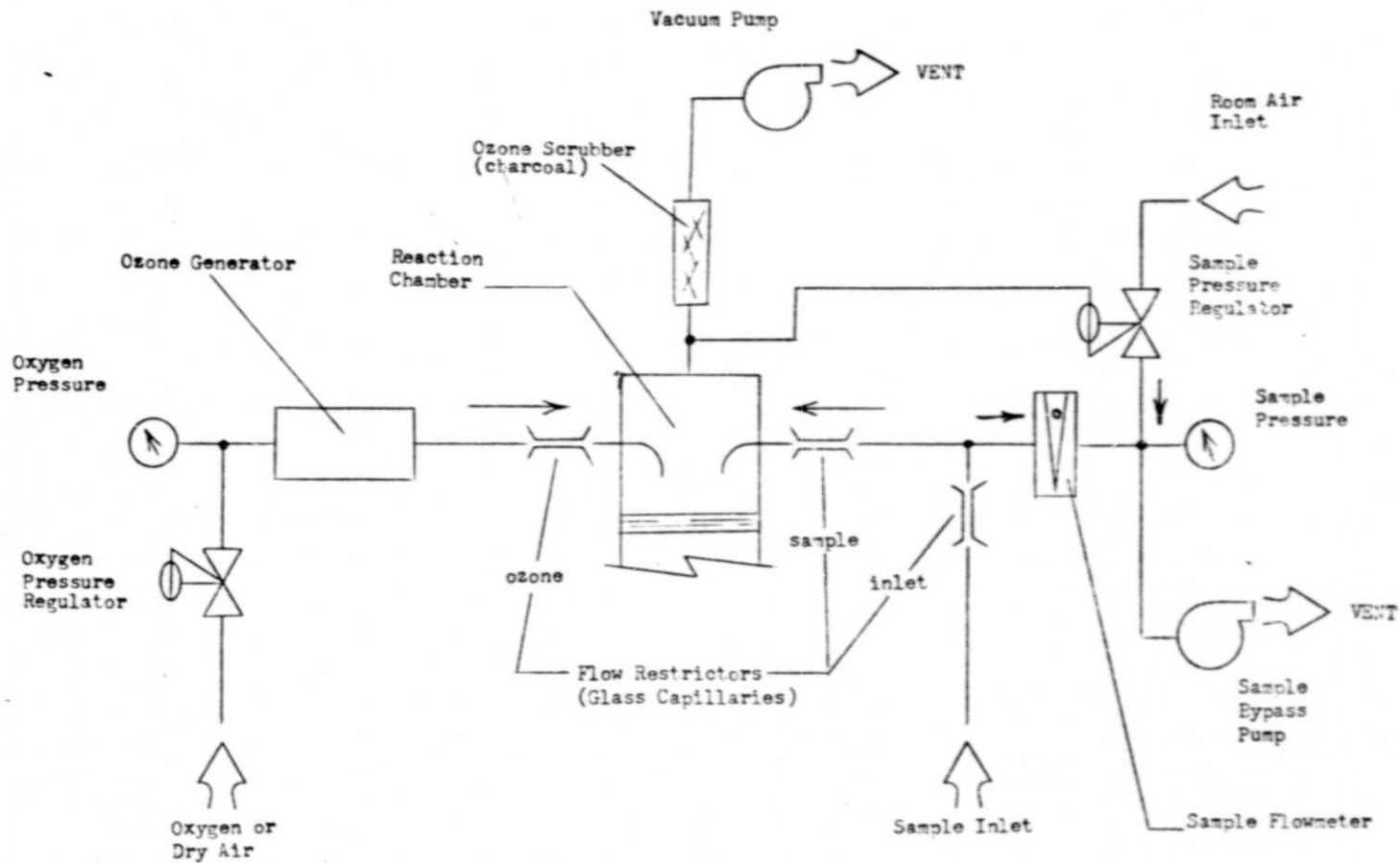FIGURE 1.   Chemiluminescent NO Analyzer; Conceptual Schematic.

FIGURE 2. Chemiluminescent NO analyzer; typical pneumatics for an analyzer of the vacuum detection type.
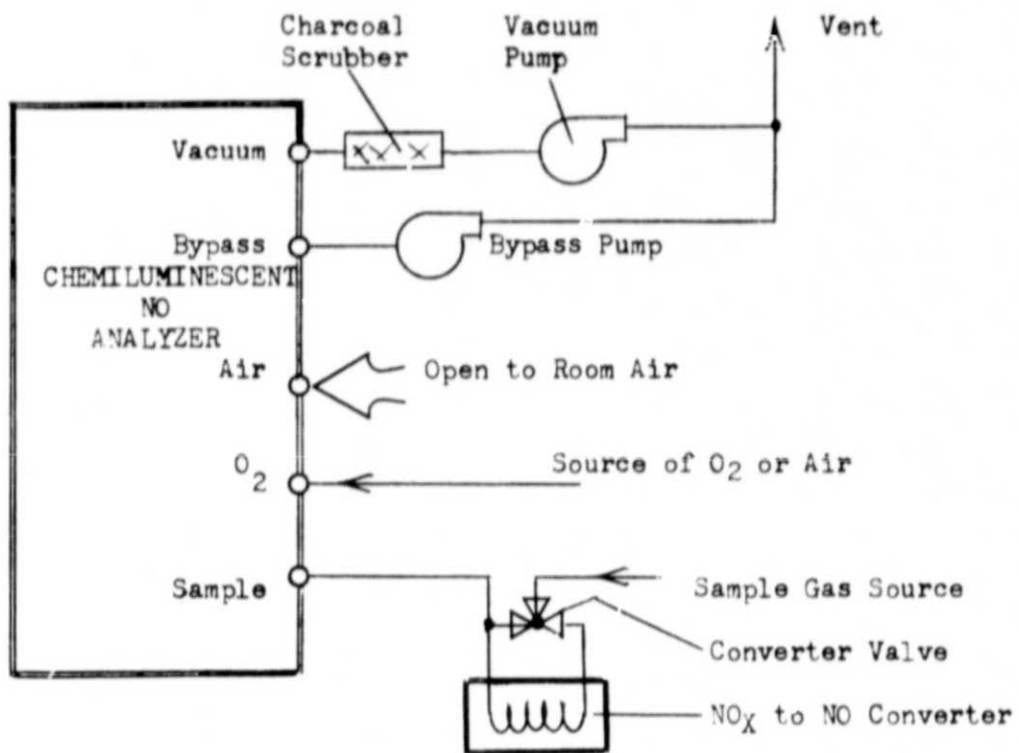
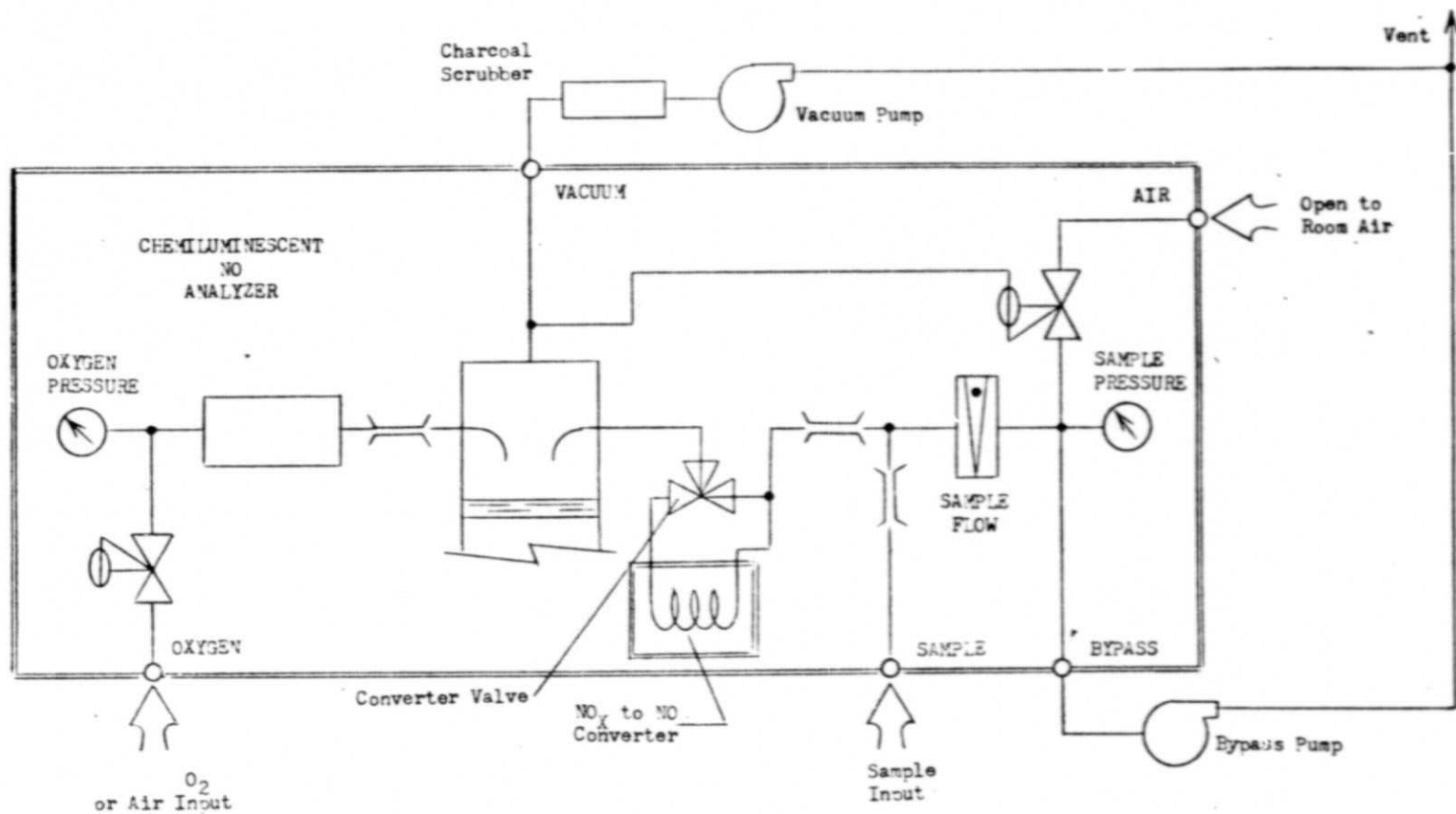FIGURE 3. Typical connection of NO_X to NO converter for upstream converter configuration.

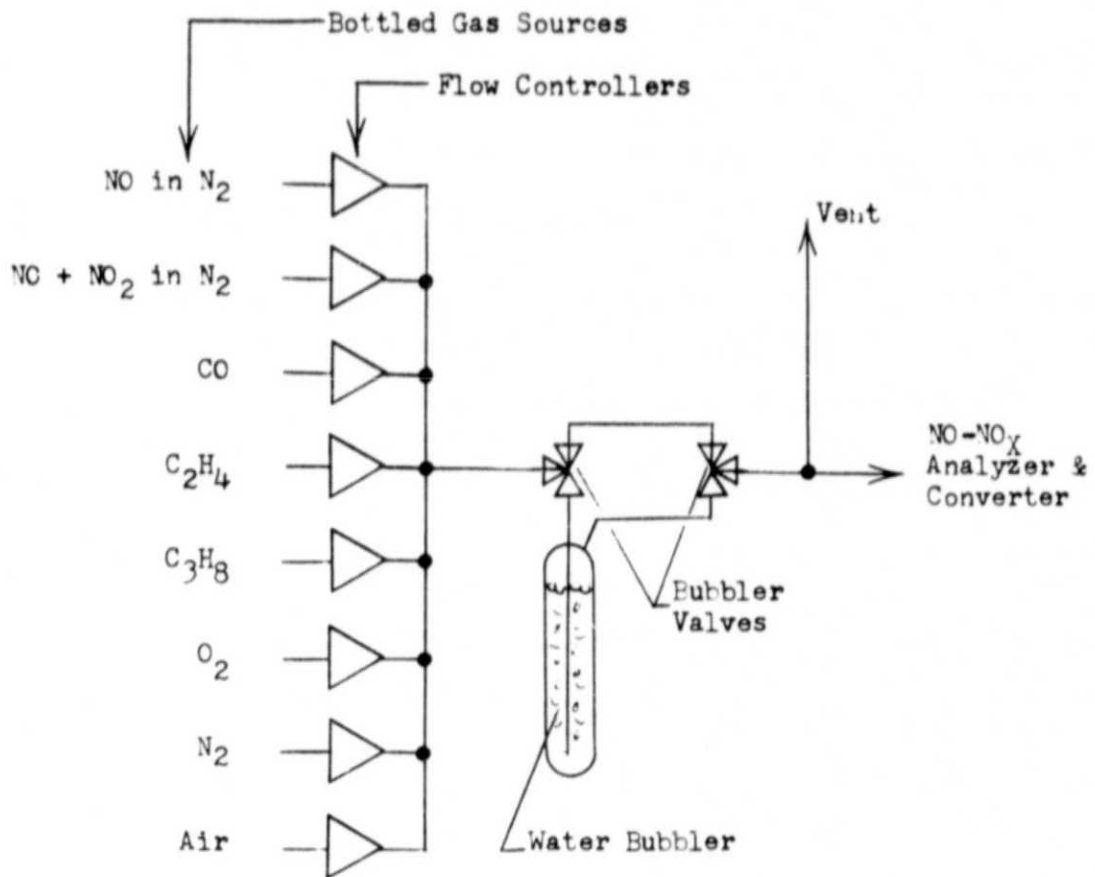FIGURE 4. Typical connection of NO$_X$ to NO converter for internal converter configuration.

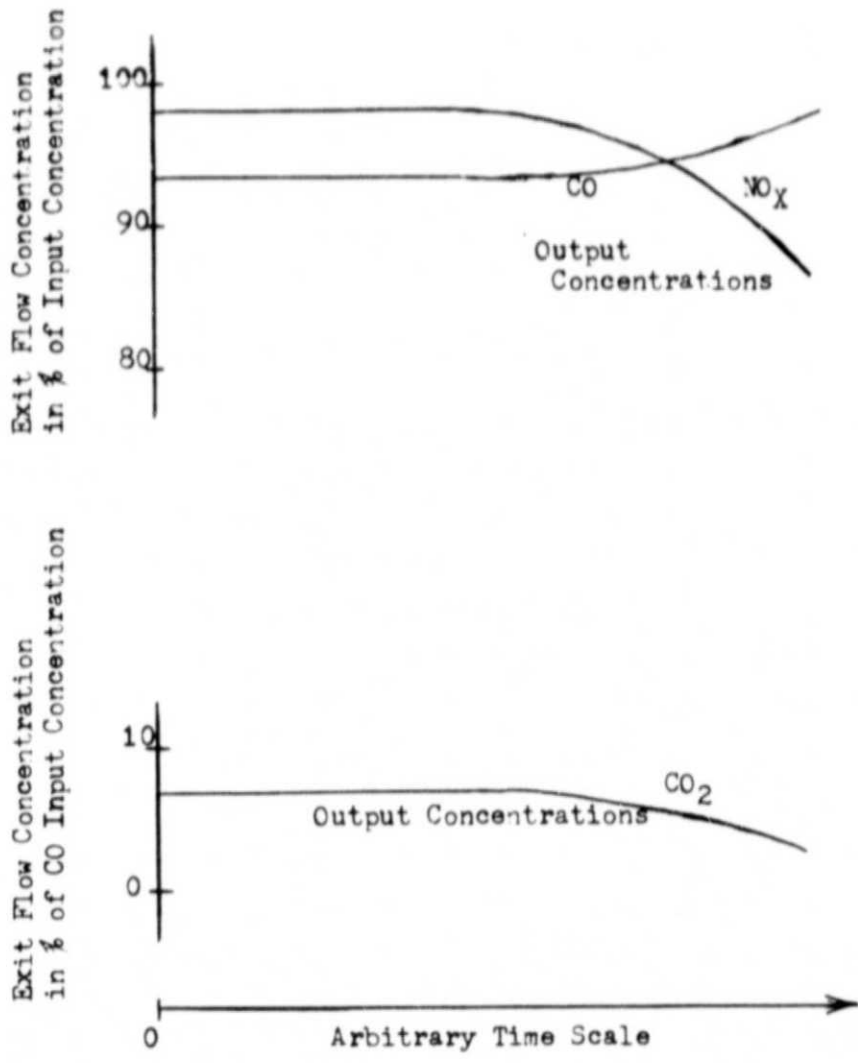FIGURE 5. Apparatus configuration for CO-NO$_X$ interaction tests.

FIGURE 6. Typical observed gas concentrations at the exit of the NO_X to NO converter for an input gas flow of CO and NO_X in N_2.
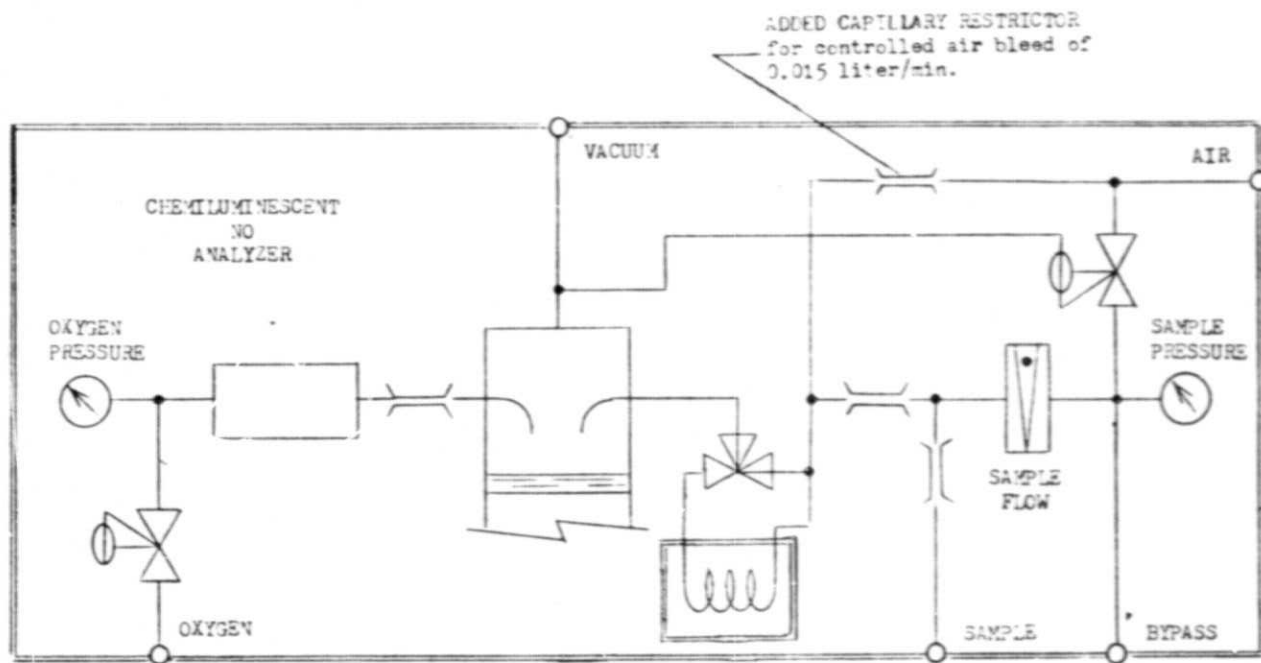
FIGURE 7. Modification of the NO-NO$_X$ analyzer (internal converter) for converter air purge.
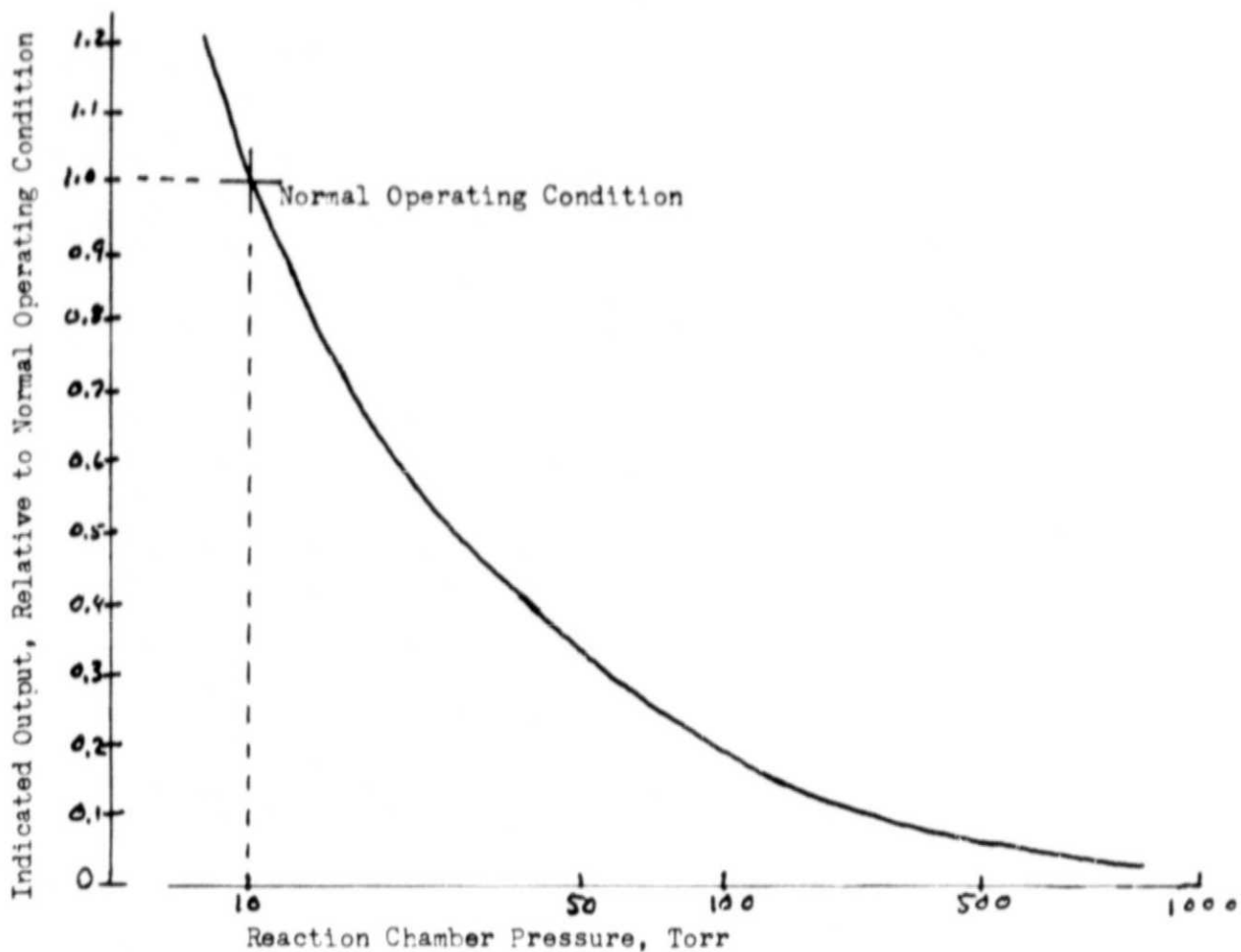
Figure 8. Chemiluminescent NO Analyzer Response as a Function of Reaction Chamber Pressure. Data taken from Reference 5.