



Reduction of nitric oxide using metal sulfide promoter mixtures and metal sulfides
by Kent Moroni Hodgson

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemical Engineering
Montana State University
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Abstract:

One of the most difficult problems in air pollution control is that of reducing nitric oxide emissions. Nitric oxide is emitted into the atmosphere where it is then oxidized to NO₂. The reduction of NO with NH₃ over a catalyst is a process which is beginning to be used in some industrial applications. However, the use of NH₃ is undesirable because of the many other industrial applications for it.

This research was concerned with using the metal sulfides BaS, CaS, SrS and FeS mixed with the chemical promoters NaF, FeCl₂, NiCl₂, CoCl₂ and Fe₂O₃ to reduce NO in an oxidizing atmosphere.

To determine if the chemical promoters reacted with NO, they were placed on the weighing pan of a Cahn R-100 continuous recording electrobalance.

The weight change was then recorded when the promoter was exposed to a gas stream containing 2.5% NO and 97.5% He. The only promoters showing a weight change were: CoCl₂ and Fe₂O₃ gained weight at 300°C and CoCl₂ lost weight at 400°C.

The reaction rates of the metal sulfide mixtures were determined using the electrobalance at 400°C and 300°C. These were determined with a gas having a composition of 2.5% NO and 97.5% He. At 400°C the fastest reaction rate was 3.155×10^{-6} moles of NO reacted per minute per gram of mixture for the BaS/FeCl₂ mixture. The FeS/FeCl₂ and BaS/CoCl₂ mixtures showed weight losses at 400°C. At 300°C the fastest rate was 4.69×10^{-6} moles of NO reacted per minute per gram of FeS/FeCl₂ mixture.

The metal sulfide promoter mixtures and metal sulfides were tested in a fixed packed bed reactor to determine how well they would remove NO from a simulated flue gas. The simulated flue gas composition was 1000 ppm NO, 1% O₂, 18% CO₂ and the balance N₂. The effluent gas was analyzed for NO using a Thermo Electron Corp. Chemiluminescent NO-NO Analyzer. A simulated flue gas flow rate of 100 ml/minute was used.

The capacities at 400°C ranged from 0 grams of NO/gram of CaS for unpromoted CaS to .0372 grams of NO/gram of FeS for the FeS/FeCl₂ mixture. The four largest capacities were FeS/FeCl₂, .0372 grams of NO/gram FeS; SrS/NaF, .0317 grams of NO/gram SrS; CaS/NaF, .0186 grams of NO/gram CaS and BaS/FeCl₂, .0168 grams of NO/gram of BaS. The capacity for FeS/FeCl₂ mixture at 300°C was .0020 grams of NO/gram of FeS.

It was determined that the presence of CO₂, SO₂ and H₂O in the simulated flue gas had no effect on the amount of NO removed by CaS at 500, 600 and 700°C. The presence of CO₂ and SO₂ in the simulated flue gas did not effect the removal of NO by the CaS/NaF mixture at 400°C. The presence of H₂O in the simulated flue gas was shown to reduce the amount of NO removed by the CaS/NaF, SrS/NaF and FeS/FeCl₂ mixtures at 400°C. The higher the concentration of O₂ the lower the NO removal capacity.

REDUCTION OF NITRIC OXIDE USING METAL SULFIDE

PROMOTER MIXTURES AND METAL SULFIDES

by

KENT MORONI HODGSON

A thesis submitted in partial fulfillment
of the requirements for the degree

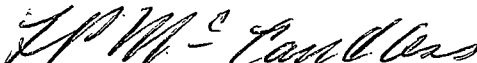
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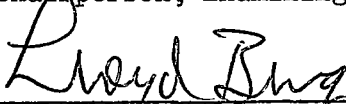
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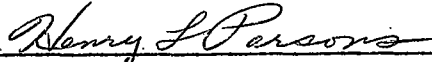
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ABSTRACT

One of the most difficult problems in air pollution control is that of reducing nitric oxide emissions. Nitric oxide is emitted into the atmosphere where it is then oxidized to NO_2 . The reduction of NO with NH_3 over a catalyst is a process which is beginning to be used in some industrial applications. However, the use of NH_3 is undesirable because of the many other industrial applications for it.

This research was concerned with using the metal sulfides BaS, CaS, SrS and FeS mixed with the chemical promoters NaF, FeCl_2 , NiCl_2 , CoCl_2 and Fe_2O_3 to reduce NO in an oxidizing atmosphere.

To determine if the chemical promoters reacted with NO, they were placed on the weighing pan of a Cahn R-100 continuous recording electrobalance. The weight change was then recorded when the promoter was exposed to a gas stream containing 2.5% NO and 97.5% He. The only promoters showing a weight change were: CoCl_2 and Fe_2O_3 gained weight at 300°C and CoCl_2 lost weight at 400°C .

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INTRODUCTION

NO_x may be the most vexing single pollutant in terms of finding an effective and cost efficient method of controlling its release. Several decades of scientists have been challenged by the difficulty of finding either a way to prevent the formation of NO or a way to render it a non-pollutant after its formation. The most common oxides of nitrogen are NO (nitric oxide), NO_2 (nitrogen dioxide) and N_2O (nitrous oxide). N_2O is an anesthetic, NO is not considered an irritant, but NO is slowly oxidized in the atmosphere to NO_2 and NO_2 is considered to be poisonous.

Nitric oxide is formed in several ways. It has been found that the NO formed in the combustion of fuels can occur by two principal mechanisms: high temperature oxidation of molecular nitrogen in the combustion air to yield thermal NO, and conversion of chemically bound nitrogen in the fuel to yield fuel nitric oxide (Lachapelle et al., 1976). The equilibrium concentration of NO with N_2 and O_2 is about 25,000 ppm at 4400°F but the equilibrium concentration is only .001 ppm at 70°F (Peters, 1971).

NO_2 is formed in a somewhat different manner. At 4400°F the kinetics of the N_2 , O_2 , NO_2 and NO reactions are such that only 5 to 10% of the NO_x formed is NO_2 with most of the rest being NO (Bartok et al., 1971). At 70°F the equilibrium between NO_2 , O_2 , and NO highly favors NO_2 . Thus, in exhaust gases most of the NO_x is NO while at equilibrium most of the NO is converted to NO_2 .

At 4400°F the formation of NO from N_2 and O_2 is very fast, while at 70°F the decomposition of NO to N_2 and O_2 is very slow. In 1917 an experiment was begun in which several containers of NO were sealed with various catalysts at ordinary temperatures. When the containers were opened in 1958 the decomposition of NO to N_2 and O_2 had proceeded so slowly that there was no N_2 detected (Shelef and Kummer, 1971). There is no thermodynamic hinderance to the thermal decomposition of nitric oxide, which is virtually complete to nitrogen and oxygen at temperatures below 1000°K. In the case of most reduction reactions the thermodynamic relations are even more favorable than for the thermal decomposition. Therefore, kinetics must be important in NO reduction and decomposition because experimentation has shown the reduction and decomposition of NO to be very slow at temperatures below 1000°K (Shelef and Kummer, 1971).

NO_2 is the most toxic of the oxides of nitrogen. Low levels of NO_2 have been shown to cause damage to plants, animals and humans. A concentration of 100 ppm for a few minutes can be very damaging to a persons health. A six month study in Chattanooga, Tenn. showed that concentrations of NO_2 of .06 to .11 ppm caused increased respiratory illnesses. Plants begin to show leaf damage at concentrations of 10-15 ppm in one hour and at concentrations of 1 ppm in 48 hours. Also, continuous exposure to concentrations of .25 ppm NO have been shown to reduce citrus crop yields (Pollution Control Technology, 1973).

NO_2 is not only dangerous in itself, it has been shown that NO_2 tends to promote the formation of such compounds as formaldehyde, acrolein and a group of plant poisons (peroxyacyl nitrates) (LaMantia and Field, 1969). Visually, NO_2 pollution may be identified by the reddish brown hue it gives to the atmosphere.

In 1976 it was estimated that 20 million tons of NO_x /year would be released into the atmosphere (Bartok et al., 1971). Stationary sources generally account for 60% of the amount of NO_x released. Some of these sources are: power plants using coal, oil and gas; industrial boiling incinerators; home heating systems and home appliances. Chemical plants where NO is produced or used and where metallurgical or high temperature processes are used are also stationary sources (LaMantia and Field, 1969). The NO_x emitted in the United States from stationary sources in 1972 is listed as follows (Mason and Shimizu, 1974):

<u>SOURCE</u>	<u>ESTIMATED NO_x EMISSIONS</u> <u>tons/year</u>
Utility Boiler	5,670,000
Reciprocating I.C. Engine	2,189,000
Industrial Boilers	2,108,000
Commercial/Residential Heating	826,000
Industrial Process Heating	390,000
Gas Turbines	291,000
Noncombustion	149,000
Incineration	<u>41,000</u>
TOTAL	11,665,000

The average United States urban concentration of NO_x in the air

is 20-25 times the natural atmospheric condition (Hopper and Yaws, 1974). The EPA has set the emission standard for coal fired steam generators at $.70 \text{ lb}/10^6 \text{ Btu}$ of heat input. This is approximately 600 ppm (Walter and Goodwin, 1974).

Oxides of nitrogen are second only to SO_2 emissions in amount of pollutants released every year. Given the large amounts of NO_x being released each year and the toxic effect of NO_2 on humans, animals and plants it is important that effective and economical means of controlling NO_x emissions be developed. The present methods of controlling NO_x emissions fall into two categories: (1) chemical reduction, decomposition or physical removal and (2) combustion modification to minimize the formation of nitric oxides (LaMantia and Field, 1969). Current research is directed toward improving these methods, to make them more efficient and more economical.

II. REVIEW OF CURRENT NO_x CONTROL METHODS

A. Combustion Modification

There are many ways in which combustion modification can be used to reduce nitrogen oxide emissions. Low excess air is one of the most promising and widely applicable combustion modification techniques for reducing nitrogen oxide emissions. By reducing oxygen availability at the burners both thermal and fuel nitric oxide can be reduced. When the technique is employed, the lowest practical excess air levels are generally dictated by a need to limit products of incomplete combustion or to prevent operating problems such as boiler vibration, slugging and fireside corrosion (Lachapell et al., 1976). Low excess air can reduce nitric oxide emissions from 30 to 50% (Pershing et al., 1975); (Crawford et al., 1975).

Flue gas recirculation is also a combustion modification technique employed. Its effect in reducing nitrogen oxide is two fold; the flame zone temperature is reduced by the recirculating flue gases, and the concentration of oxygen available for nitric oxide production is reduced. This modification can be expensive due to the need for a high temperature fan and additional duct work (Lachapelle et al., 1976). Flue gas recirculation can reduce nitric oxide emissions as much as 30% (Pershing et al., 1975) (Henry et al., 1975).

Water or steam injection reduces thermal nitric oxide because it reduces the flame temperature. Installation costs are low; however, water injection will impose an efficiency penalty (Lachapelle et al.,

1976); (Blakeslee and Burbach, 1975). Staged combustion has also been shown to reduce nitric oxide emission (Armento and Sage, 1975). In staged combustion the burners may be staggered fuel rich and either fuel lean or air only. This modification is applicable to all fuels, especially coal. However, load reduction can result and there may be fireside corrosion problems (Lachapelle et al., 1976).

Reduced air preheat temperature lowers combustion zone peak temperatures and reduces thermal nitric oxide emissions (Pershing et al., 1975) (Armento and Sage, 1975).

Load reduction causes a decrease in combustion intensity and peak temperatures which causes a reduction in the amount of thermal nitric oxide produced (Armento and Sage, 1975) (Blakeslee and Burbach, 1975). This modification is not consistent with today's energy needs. Progress has been made in reducing nitric oxide emission through improved burner design. Several promising low nitric oxide (150 to 300 ppm) burner configurations for use in wall fired pulverized coal boilers have been identified. Scale-up criteria must still be developed (Lachapelle et al., 1976). Rocketdyne Division of Rockwell International is developing an optimum distillate oil burner for residential and commercial applications. The design has reduced NO levels from 50 to 65% of those from conventional burners and is capable of smoke free operation in 10% excess air (Dickerson and Okuda, 1974).

Stack gases from oil and coal-fired power plants are known to be major sources of NO_x (Bartok et al., 1969). A significant fraction of the NO derives from the reaction of nitrogen with oxygen at high temperatures. This NO production can be greatly reduced by combustion modification (Bartok et al., 1969). It has been shown, however, (Pershing et al., 1975; Turner et al., 1972) that the NO deriving from the nitrogen content of the fuel is still well above desirable limits in spite of combustion modification. The high nitrogen content of coal makes its use undesirable in this respect. The need to develop processes to control NO_x emissions is thus clearly established.

B. Chemical Reduction, Decomposition or Physical Removal

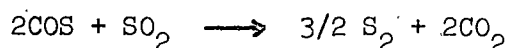
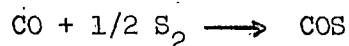
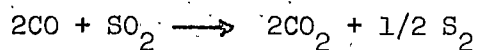
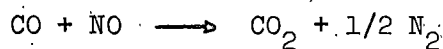
TRW Systems has conducted a technical and economic assessment of various catalytic schemes for nitrogen oxide control for stationary power plants (Lachapelle et al., 1976). On a laboratory scale with simulated flue gas, catalytic reduction of nitric oxide was studied over a range of space velocities from 5000 hr^{-1} to $20,000 \text{ hr}^{-1}$ (standard temperature and pressure) and temperatures from 200°C to 450°C . Approximately forty-five catalysts were screened to determine nonselective nitric oxide reduction with hydrogen and carbon monoxide and selective reduction with ammonia, hydrogen and carbon monoxide. Identified as being the most promising for selective reduction with ammonia are iron-chromium, vanadium, copper-lead, molybdenum and platinum catalysts. Parametric studies have obtained nitric oxide conversion of about 60 to

90% with ammonia stoichiometry about 1.0, temperature 400°C, space velocities of 5,000 to 20,000 hr⁻¹, and inlet nitric oxide concentrations of 250 to 1000 ppm (Lachapelle et al., 1976). Ammonia has been the only reductant purported to show true selectivity for the heterogeneous reduction of nitric oxide to nitrogen in the presence of excess oxygen. Mitsubishi Petrochemical Co., Ltd. and Hitachi Ltd. (Toyko, Japan) have developed a metal oxide catalyst which when used with ammonia can reduce nitric oxide emissions from industrial plants. The nitric oxide is changed with the ammonia to water and nitrogen. This process works efficiently at 250-300°C and removes over 90% of the nitric oxide. This process meets Japan's NO_x standards which are much stiffer than those of the United States (Environ. Sci. & Tech., 1975). Hitachi Ltd. has also developed a catalyst which can decompose NO_x in stack gases at temperatures of about 100°C. This decomposition is done with a catalyst of activated carbon pellets treated with ammonium chloride, bromide or iodide and packed in a column. Ammonium bromide is the most effective of the three halides, and gave 80% NO_x removal at 100°C and 97% removal at 130°C. Over several months of tests, no change in NO_x removal or release of bromine was observed. The output gas is nitrogen and water vapor. The same catalyst removes SO₂ at a high rate, with ammonium sulfate as a product. High oxygen and low water vapor concentrations increase the reaction rate (Environ. Sci. & Tech., 1975).

Iron oxide supported on alumina is a promising catalyst/absorbent

for use in the simultaneous removal of NO_x and SO_x from power plant stack gases. A dry-contacting process is under development which would operate under net reducing conditions at temperatures of 370°C to 540°C . Iron oxide is converted to the ferrous state, NO is reduced to N_2 or NH_3 , and SO_2 is removed as ferrous sulfide or sulfate. Regeneration with air produces SO_2 and reforms Fe_2O_3 (Clay and Lynn, 1975).

A dual bed catalyst system for the simultaneous reduction of SO_2 and NO has been developed by Sood and Kettrell (1974). The reactions:



are considered to take place in this system. To get 90% removal stoichiometric quantities are necessary and the catalyst bed temperature must be controlled very carefully.

At Montana State University, Evoniuk (1978) has developed a process using mixtures of alkali carbonates and transition metal oxides to absorb dilute concentrations of NO (800 ppm to 10,000 ppm). The NO is then desorbed in a concentrated stream.

Shell Oil Company has developed a flue gas desulfurization process using a fixed bed reactor of unusual design. This design eliminates

high pressure drops, plugging and acceptor contamination by the fly ash. The acceptor is copper supported on alumina, and contamination of the acceptor with particulate is avoided by causing the flue gas to flow alongside the acceptor mass rather than through it. In this arrangement, the gas passes through open channels with the result that the pressure drop is low and particulate does not accumulate in the acceptor. The acceptor is contained by gauze in a large number of flat, thin layers with passages in between for the flue gas; the sulfur dioxide in the flue gas reaches the acceptor by diffusion (Groenendaal et al., 1976). This reactor design may be of use with metal sulfides in controlling NO_x emissions.

Earlier in this section several processes were discussed for reducing NO_x emissions. Most of these have not passed the laboratory scale of development. Some of these processes appear to be nearing industrial application. Those reducing the NO using NH_3 over a catalyst appear to be promising. The major disadvantage of NH_3 reduction processes is that if some of the NH_3 is not reacted and is released, it becomes an air pollutant. Reduction using NH_3 is used quite a bit in Japan on an industrial scale; however, NH_3 is an expensive reactant. In 1972 it was estimated that 11,665,000 tons of NO_x were emitted from stationary sources (Mason and Shimizu, 1974). If this were all reduced using NH_3 , 2,874,000 tons of NH_3 would be required. This represents 18.9% of the 1972 production of NH_3 (U.S. Bureau of the Census, 1974).

NH_3 is in great demand as a raw material for many industries. Therefore, if an alternate method of reducing NO could be developed it would probably be economically advantageous. A new and better method is needed for NO_x control. The reduction of NO using metal sulfides may provide this method.

C. Reduction With Metal Sulfides

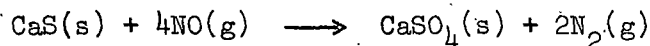
It was shown by White (1973) initially that metal sulfides will reduce nitric oxide. Complete reduction was attained over a temperature range of 400°C to 800°C . The metal sulfides used were aluminum sulfide, antimony trisulfide, barium sulfide, cadmium sulfide, calcium sulfide, cupric sulfide, cuprous sulfide, ferric sulfide, lead sulfide, molybdenum disulfide, strontium sulfide, sulfurated potash, tungsten disulfide and zinc sulfide. Of these, White recommended barium sulfide, bismuth sulfide, cadmium sulfide, calcium sulfide, cuprous sulfide, ferric sulfide, molybdenum disulfide, strontium sulfide and zinc sulfide for further study. White also successfully lowered the temperature for the reduction of NO by the addition of various chemicals; the temperature range was lowered to 400°C to 500°C . The most promising additives were K_3FeF_6 , $\text{K}_3\text{FeF}_6/\text{NaCl}$ and NaF . It was also shown that NO would be reduced in the presence of O_2 and that the presence of water vapor did not appear to deter the reduction of NO. White also determined that in the reduction of NO with calcium sulfide, the solid product was at least

80 weight percent calcium sulfate.

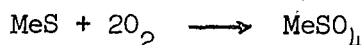
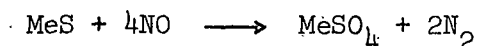
Erickson (1974) studied the reduction of NO using CaS impregnated on high surface area supports. The results of the support material tests showed that Harshaw 1602 1/8 inch pellets of alumina and silica gave good reduction of NO without forming any undesirable products such as H₂S or SO₂. Nalco 2910-B 1/8 inch pellets of mostly alumina gave good reduction of NO, but caused the formation of some H₂S. Alcoa T-71 1/4 inch to 8 mesh tabular alumina gave very poor reduction of NO, but no H₂S or SO₂ was formed. Linde TM-0-1114 1/8 inch molecular sieves, which are synthetic crystalline metal alumina-silicates with Na as the metal in this case, gave good reduction of NO, but it caused the formation of SO₂.

In testing NiS as a reducing agent, Erickson found that SO₂ was produced along with the reduction of NO. In working with contaminants in the NO gas stream, it was found by Erickson that H₂O produced small amounts of H₂S and decreased the reduction of NO. The presence of H₂ seemed to increase the reductions of NO by CaS but caused the formation of H₂S. Natural gas also produced H₂S but did not seem to effect the reduction of CaS. He also found that O₂ and CO₂ did not effect the reduction of CaS.

McIntyre (1974) used a continuous recording electrobalance in studying the reaction



and found that the global rates for the reaction of CaS on high alumina Harshaw pellets increased from $.25 \times 10^{-4}$ at 390°C to $.45 \times 10^{-4}$ moles of CaSO_4 formed per hour per gram of pellet at 493°C . Linde molecular sieves gave greater average rates. Rates varied between $.32 \times 10^{-4}$ and $.64 \times 10^{-4}$ moles CaSO_4 formed per hour per gram of pellet for three temperatures between 392° and 438°C . The pellets impregnated with CaS were approximately 5 wt.% CaS. McIntyre also determined that at 440°C and with a flow rate ranging from .12 std. cm^3 per second to 3.8 std. cm^3 per second external film diffusion was not important for the reaction using Harshaw pellets. It was also shown by McIntyre that the rate of reaction of CaS with O_2 is greater than the rate of reaction of CaS with NO. The reaction rates of the two following reactions:



were determined by Hodgson (1975) using a Cahn R-100 continuous recording electrobalance. The rates of reaction of NO with metal sulfides were determined using a gas with a composition of 2.5% NO and 97.5% He. The rate of reaction of O_2 with metal sulfides was determined using a gas mixture with a composition of 2.5% O_2 and 97.5% He. In general, the rate of reaction of the metal sulfide with oxygen was faster than with NO for all temperatures tested. Over the temperature range of 300°C to 500°C the reaction rates with NO ranged from no reaction for ZnS at 400°C

and 500°C and no reaction for Cu_2S at 500°C to 5.48×10^{-6} moles of NO reacted per minute per gram of FeS at 500°C. The reaction rates of O_2 ranged from no reaction with CaS and BaS at 300°C to 7.49×10^{-6} moles of O_2 reacted per minute per gram of BaS at 500°C. Based on this study, it was recommended that BaS , FeS , SrS and CaS be studied further to see if they might provide a method to reduce NO_x emissions.

III. PURPOSE OF RESEARCH

The purpose of this research is to further investigate the possibility that metal sulfides, in this case BaS, CaS, SrS and FeS, with various chemical promoters may provide an economical and efficient solution to the NO_x emissions problem.

Specifically this study is concerned with:

- (1) The ability of powdered metal sulfides (BaS, CaS, SrS, and FeS) mixed with various chemical promoters (NaF, NiCl₂, CoCl₂, FeCl₂ and Fe₂O₃) and placed in a fixed packed bed to remove NO from a simulated flue gas.
- (2) The effect of temperature on the ability of these mixtures to remove NO_x.
- (3) The effect the presence of CO₂, SO₂ and H₂O in the simulated flue gas will have on the amount of NO removed.
- (4) The possibility of using a metal sulfide impregnated on a high surface area support to remove NO.

IV. APPARATUS

Figure 1 shows a schematic diagram of the apparatus used with the tubular reactor. Four rotameters were used to mix the feed gas stream. A typical coal fired steam generating plant flue gas stream composition was used. The feed gas was usually 1000 ppm NO, 1% O₂, 18% CO₂ and the remainder was N₂. A reactor bypass was included so that the feed stream NO_x composition could be determined directly with the analyzer. The feed gas was fed into the top of a 5/8 inch diameter stainless steel pipe reactor. The reactor is shown in Figure 2. The reactor consisted of two sections; the top 8 inches were packed with stainless steel rings and functioned as a gas preheat section. It was connected to the bottom section by a 1 1/2 inch piece of 1/2 inch inside diameter stainless steel pipe. The bottom section was 11 1/2 inches long and contained a porous stainless steel disk about one inch from the top of the bottom section. The packed bed was placed on this disk. Directly under the disk was a 1/4 inch outside diameter stainless steel thermowell into which an iron-constantan thermocouple was placed. The gas entered the top of the reactor and left the bottom. A glass wool filter and a heat exchanger were placed directly after the reactor to prevent any of the powdered sulfide from escaping and to cool the gas stream. The gas stream then passed to the analyzer which was a Thermo Electron Corporation Model 10A Self Contained Chemiluminescent NO-NO_x Analyzer.

A rotameter was also provided that would bleed air or N₂ directly into the analyzer. This was to dilute the NO_x if its concentration was

