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ESL-TR-84-41

Transformation of Nitrogen Oxides While Sampling Combustion Products

J.W. GROVE

G.S. SAMUELSEN

FEBRUARY 1985

FINAL REPORT

SEPTEMBER 1978 - DECEMBER 1983

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The objective of the program was to assess the condition under which transformations of nitrogen oxides (NO and NO_2) may occur in an extractive probe used to sample exhaust gases from combustor sources such as gas turbine engines and boilers. The approach was to use simulated combustion products in a controllable laboratory experiment. Trials were run using 2-meter (79-inchs) long, 6.35 mm (0.25-inch) OD tubing. Tubing materials considered included type 316 stainless steel, quartz, inconel, and nickel. Various gaseous compositions, including those representative of gas turbine exhausts, were evaluated for various temperatures over a range ($150^{o}C$ to $400^{o}C$) typical of the temperatures experienced by probe materials in practical systems.

NO_x is conserved in 316 stainless steel and quartz tubes up to $400^{o}C$. Above $400^{o}C$, NO_x can be destroyed.

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The ratio of NO_2/NO is conserved up to $300^\circ C$ in 316 stainless steel and $400^\circ C$ in quartz. The present results were not changed appreciably by the presence or absence of water with one notable exception. In the stainless steel, the reactivity of the probe (reduction of NO_2 to NO) was significantly increased above $300^\circ C$ (20- to 85-percent at $400^\circ C$) when both oxygen and high levels of hydrocarbons were present.

Stainless steel is more rugged than quartz and, as a result, more commonly used as a sampling probe material. The exploration of alternative metallic tube materials, such as nickel and inconel, was not successful in identifying a durable tube material that was less reactive than 316 SS. Both nickel and inconel were more reactive.

Based on the results of this study, quartz is the most desirable material to use for sampling at elevated temperatures. Quartz was inert to all the sample compositions and sample temperatures explored in the present experiment. The one practical exception to the use of quartz is the vulnerability to breakage. Stainless steel tubes with quartz glass linings, available commercially, represent a reasonable solution where sample integrity is a major objective and reasonable handling of the probe can be maintained.

Should quartz or quartz-lined stainless steel not be an option, then type 316 stainless steel is a reasonable alternative. However, if stainless steel is used at temperatures exceeding $200^\circ C$, the tube should be water-cooled to ensure maintenance of sample integrity. Care must be excercised to cool the tube with hot water ($> 60^\circ C$) to ensure that water in the combustion products does not condense.

PREFACE

This report summarizes work done between September 1978 and December 1983. Dr. Scott Samuelsen, the principal investigator, discovered an inconsistency in the TURBINE matrix data; it was associated with the delicacy with which propanol and methanol have to be added to the carrier gas. The experimental set-up was changed and the TURBINE data set reproduced. This second data set was consistent with the findings in the first, and the reproduction of the measurement was very satisfactory. The key difference the second time was the confidence in the levels in the propanol and methanol added to the carrier. This report does not reflect the challenge in the design of the experiment and development of a successful experimental protocol. The report addresses the suitability of stainless steel, quartz, inconel, and nickel for sampling probes to measure nitrogen oxides.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

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SECTION I

INTRODUCTION

To assess the conditions under which transformations of nitrogen oxides (NO and NO_2) may occur in a gaseous sample probe, a controllable laboratory experiment was designed and used in an earlier study to systematically establish the conditions under which NO and NO_2 could be transformed and the extent of transformation (References 1, 2, 3, and 4). Under an AFOSR program at the UCI Combustion Laboratory (Grant 78-3586), the Environics Division of the Air Force Engineering and Services Center (AFESC/RDV) provided supplemental funding to modify the experiment to (1) include water vapor in the simulated combustion products, (2) provide more precise control over the temperature and history of the pollutant mixture prior to sampling, and (3) simulate gas turbine exhaust products as well as reacting zone gases, automobile exhausts, and boiler flue gases.

The experiment was successfully modified and operated. Various compositions of simulated exhaust gases, including those representative of gas turbine exhausts, were run through sample probes of varying materials and analyzed for nitrogen oxide transformations. This analysis was performed for various probe temperatures over a range (150°C to 400°C) typical of the temperatures experienced by probe materials in practical systems.

Trials were run using 2-meter (79-inchs) long, 6.35 mm (0.25-inch) OD tubing, and performed with and without water addition. Quartz and stainless steel (type 316) were the principal materials evaluated although Inconel-600 and Nickel-200 were considered as well. Type 316 stainless steel (316 SS) is the material commonly used for sampling purposes. Tubing stock and fittings are readily available, 316 SS is durable yet easy to bend during fabrication, and the stainless quality is resistant to corrosion. However, this resistance does not preclude surface reactions that could alter the composition of a sample. Quartz tubing, in contrast, is inert to surface attack and, as a result, is attractive for sampling. However, the vulnerability of quartz to breakage renders the material impractical except for the most controlled conditions. To assess whether durable, metallic tubes are available which are less reactive than 316 SS to sample composition transformation, two nickel-containing tube materials were selected: a nickel tube (Nickel-200) and an alloy of nickel (Inconel-600). An investigation of stainless steel composition indicated that the nickel content may be associated with an increase in resistivity to transformation (Reference 3).

SECTION II

EXPERIMENTAL METHODS

A. CARRIER GASES

Carrier gases representative of boiler and automotive exhaust, as well as combustor reaction zones, are herein referred to as STANDARD carriers; those representative of turbine jet engines are referred to as the carrier TURBINE. Compositions and concentrations of the carriers, presented in Table 1, were established, based upon surveys of practical devices (References 1, 2, 3, and 4). All STANDARD carrier gases (exclusive of water and propylene) were mixed and supplied in gas cylinders by a commercial vendor. Propylene and water, if selected, were added during the experiment. The TURBINE carrier gas was also supplied by a commercial vendor except for the water, methanol, and propanol, each of which was added in the conduct of the experiment. The baseline composition was selected, based on exploratory tests, as the condition for which NO and NO_2 transformation was most likely.

B. THE EXPERIMENT

The experimental system is shown in Figure 1. The experiment is performed in three steps: gas preparation, probe exposure (with sampling before and after the exposure), and analysis.

1. Gas Preparation

The appropriate carrier gas composition is selected by means of a toggle switch located on the control panel. Upstream carrier gas pressures are maintained constant to generate a steady flow of 7 ℓ/min. The bulk of the flow is bubbled through three 500 ml fritted glass water towers to ensure saturation if water addition ("wet trial") is to be performed. The temperature of the water in the towers is set and maintained constant for each trial to achieve the desired water concentration. For a dry trial, the carrier flow is routed around the water towers. For the TURBINE tests, a portion of the carrier is routed through 1-liter Erlenmeyer flasks used to house liquid methanol and propanol.

Enroute to the furnace from the water towers, heating tape is wrapped around the Teflon® tubing to prevent premature water condensation. In a Lindberg Model #51828 furnace, the carrier gas is circulated until it reaches the set furnace temperature. At this point, the carrier stream enters a mixing venturi – where the pollutant gases (NO, NO_2, and C_3H_6 if selected) are introduced in the proper amounts from high-concentration sources by means of flow restrictors. A sample (3ℓ/min) is extracted immediately after mixing is completed. (This sample location is referred to as SP2.) A flow of 4ℓ/min is run though the probe to be tested. At the end of the probe, another 3ℓ/min sample is extracted at sample point SP3, leaving 1ℓ/min to vent.

Temperatures are monitored at SP2, SP3, in the furnace, and just downstream of the water towers; pressures are monitored at SP2, SP3, and just upstream of the water, methanol/propanol addition system. In addition, the carrier gas flow rate is monitored just upstream of the water/methanol/propanol addition system.

TABLE 1.   NO SAMPLING CARRIER GAS COMPOSITION

Carrier	Composition					
	CO_2 %	O_2 %	H_2O %	HC ppm	NO ppm	NO_2 ppm
STANDARD	12	5	0, 14	0	500	75
	12	5	0, 14	500 propylene	500	75
	12	0	0, 14	500 propylene	500	75*
	12	0	0, 14	0	500	75
TURBINE	4	14	0, 5	18 methane 0.5 butane 34 ethylene 12 propylene 2.5 I-butene 30 methanol 3 propanol	500	75

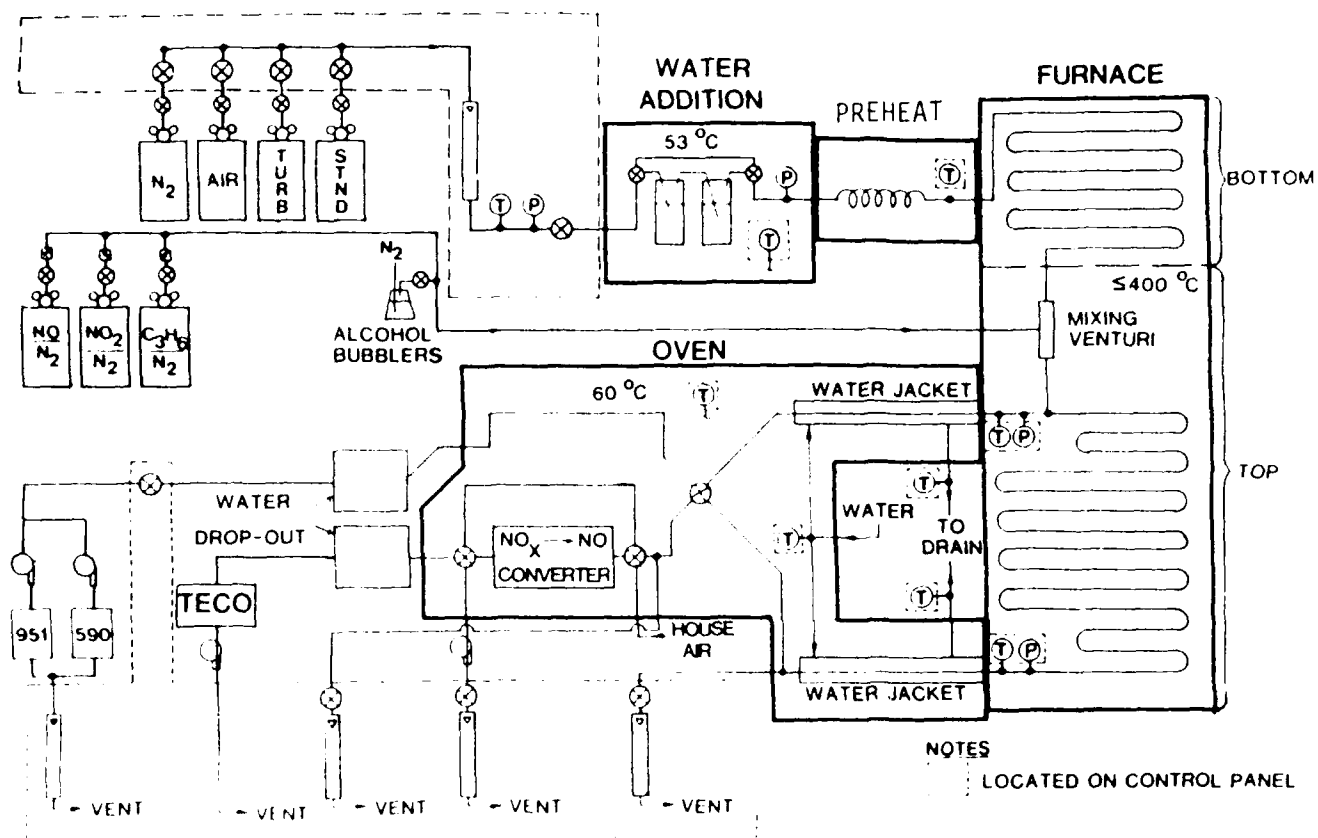* Baseline composition (0-percent O_2, 500 ppm HC, 0-percent water)

Figure 1. Experimental System

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The samples from SP2 and SP3 are immediately cooled by water jackets in a specially designed water-cooled quartz extractor to 60°C, and transported through the furnace wall and into a Blue M oven maintained at 60°C. The oven houses various solenoids as well as a carbon $NO_2 \rightarrow NO$ converter. Monitored temperatures include that of the oven, of the cooling water at SP2, SP3, and at the mixing venturi, and of the converter. The NO_x converter jacket temperature is controlled by a constant input voltage from a variac, and the cooling water flow rate is monitored by a rotameter just upstream of the Blue M oven.

2. Probe Exposure

Instrumentation used to analyze the samples includes a TECO Model 10 AR Chemiluminescent $NO-NO_2-NO_x$ Analyzer, a Beckman Model 951 NO/NO_x Analyzer, and a Beckman Model 590 HC/CO Analyzer. From the control panel, the SP2 and SP3 samples can be routed, by means of a solenoid off-on switch, to the TECO or to the Beckman 951. In addition, the TECO sample can be routed through or around the converter. By the use of metering valves and rotameters (located on the control panel) as well as by vents, proper flows through the probe and to the instruments are maintained regardless of the sample path. For the trials in which propylene is introduced, a small portion of the Beckman 951 sample is extracted and routed to the Beckman 590. Water is condensed out of the samples before transportation to the analyzing instruments by means of ice baths.

3. Analysis

The experiment is run in the following manner: with the appropriate carrier gas selected, the desired concentrations, if any, of water and methanol/propanol are added, and the NO, NO_2 and C_3H_6 (if selected) are introduced at 55°C to the carrier stream at the venturi port. The temperatures of the cooling water at SP2, SP3, and at the mixing venturi, of the oven, of the converter, and of the gas just downstream of the water towers are noted. The furnace is set at 150°C and, when this temperature is achieved, the temperature of the furnace, and the temperatures and pressures of SP2 and SP3 are recorded. The following data are collected: A TECO analysis of the SP2 sample with the converter off; TECO analysis of the SP3 sample with the converter off; Beckman 951 analysis of the SP2 sample, TECO analysis of the SP2 sample with the converter on; and TECO analysis of the SP3 sample with the converter on. The furnace temperature is then incremented 50°C (up to 400°C) and the readings above are repeated. At least four successive probe trials are necessary for the probe response to stabilize.

SECTION III

RESULTS

A. TEST MATRIX

The combinations of sample probe materials and carrier gas compositions
are presented in Table 2. The parameters evaluated were probe exposure
cycles, probe preconditioning, carrier composition, presence of water, and
probe material.

B. PARAMETERS

1. Probe Exposure Cycles

The probes tested are repeatedly cycled through the temperature range
described above until a steady-state response is achieved. The chemical
transformation observed for all tests conducted is the reduction of NO_2 to
NO. "Reactivity" is associated with the change of NO/NO_2 concentrations from
the probe inlet (SP2) to the probe outlet (SP3). If NO_2 reduction is
experienced in a particular trial, the probe is said to be reactive, with
reactivity varying from low to high depending on the extent of NO_2 reduction
and the temperature at which it first occurs. The concentration of NO_x (NO +
NO_2) is also monitored and found to be conserved in all the tests reported
here although in previous work, as noted below, destruction of NO_x was
observed at the elevated test temperatures.

An example of sequential exposure cycles of a 316 stainless steel probe
is presented in Figure 2a for the baseline case in the STANDARD matrix. The
initial reactivity of the probe is very high (Cycle 1) with an 80-percent
reduction of NO_2 to NO and the first evidence of change at 250°C. By the
fifth cycle, the NO_2 reduction stabilizes to approximately 40 percent, and the
first evidence of change occurs at 350°C. This behavior is typical of all the
metal probes tested. Generally, three to five cycles are required for a
repeatable response to be achieved. In contrast, quartz exhibits no change
from that measured for the first cycle (Figure 2b).

2. Probe Conditioning

For the results reported below, the probes tested were tested as received
from the supplier. However, preliminary tests were conducted on 316 stainless
steel to evaluate the effect of washing the probes prior to testing. The
probes were first washed with trichlorylethylene, rinsed with methanol, and
dried at room temperature. Probes washed in this fashion proved to be more
reactive. Extensive discussions with manufacturers of stainless steel tubes
lead to the conclusion that this washing procedure removes residual dirt and
grease from the inner tube surface, thereby exposing more sites to contribute
to the initial reactivity. The decision to use probes as received (rather
than washed) for the principal tests was predicated on the likelihood that
those probes used in practical systems are installed as supplied.

TABLE 2. PROBE TYPES AND CARRIER COMPOSITIONS TESTED

Probe Type	Case	Carrier							
		STANDARD						TURBINE	
		O_2, %		HC, ppm		Water, %		Water, %	
		0	5	0	500	0	14	0	5
316 SS, or	1	•		•		•			
Quartz	2	•		•			•		
	3		•	•		•			
	4		•	•			•		
	5	B[a]			B	B			
	6	•			•		•		
	7		•		•	•			
	8		•		•		•		
	9							•	
	10								•
Inconel-600, or Nickel-200	11	B			B	B			

[a] Baseline composition

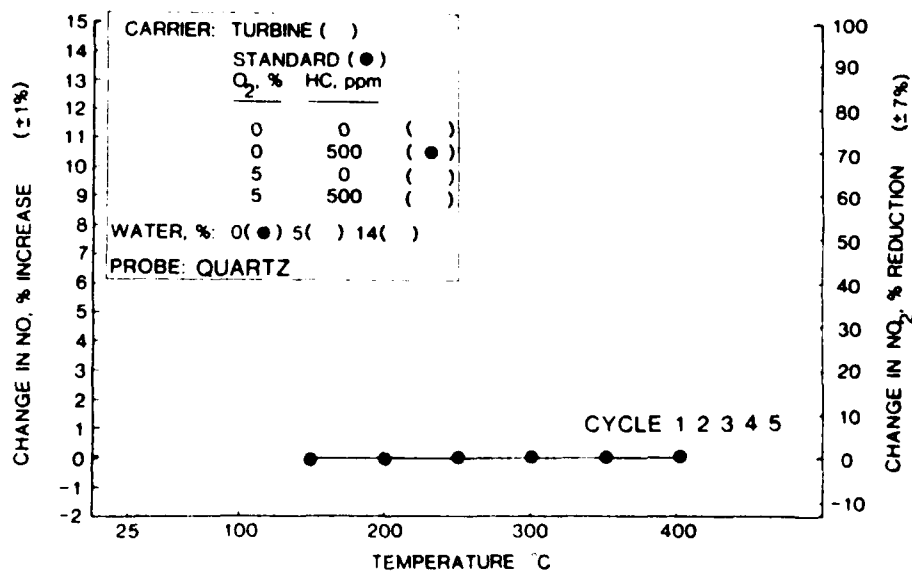a) 316 Stainless Steel Probe
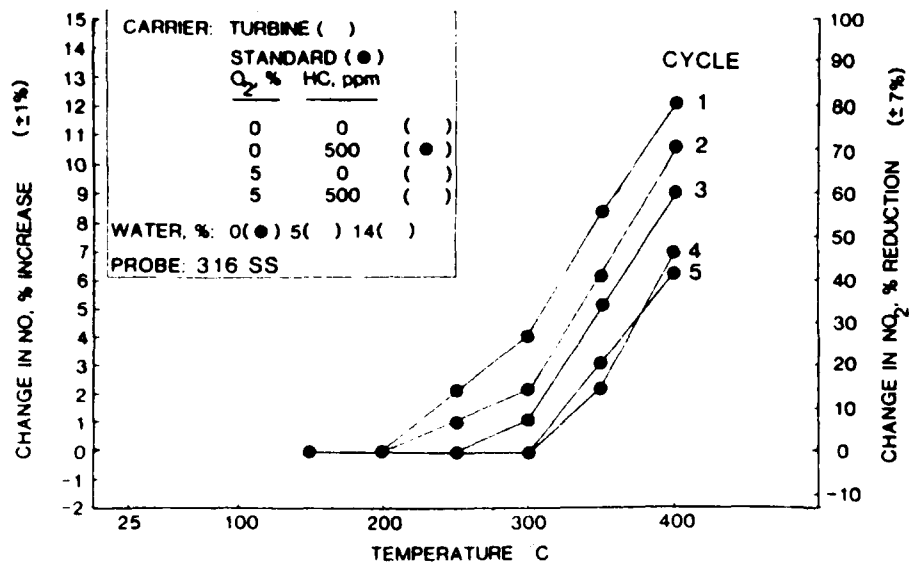
b) Quartz Probe

Figure 2. Sequential Exposure Cycles

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3. Carrier Composition

The composition of the carrier gas was found to be a major factor in establishing the reactivity of the 316 stainless steel. The results for the STANDARD carrier (Table 1) are summarized in Figure 3a. The reactivity is highest for the baseline case, lower for the case where both oxygen and propylene are present, and inconsequential in the absence of the propylene (for both 0 or 5 percent oxygen). In contrast to the 316 stainless steel, the quartz tube is virtually nonreactive for all STANDARD carrier compositions (Figure 3b). It is noteworthy that the 316 stainless steel and quartz reactivities are less than those observed and reported from the earlier experiment (Reference 4), an example of which is presented in Figure 4. Two factors lead to the higher reactivities in the previous work. First, the temperature was not controlled as well as in the present experiment. The probe was heated in a Lindberg tube furnace rather than in the current box furnace. As a result, the probe experienced uneven heating. An investigation of the heating variation revealed that, at a 400°C set point, the probe could locally heat to 600°C at locations where the tube was in the near vicinity of the heated filament. The design of the present experiment ensured that the temperature of the probe was maintained isothermal at the set point. Second, the sample extracted at SP2 and SP3 was not immediately cooled in the previous experiment and reaction could persist in the sampling tube. In the present experiment, the design of the sample ports included water-cooling to immediately quench the reaction.

The results for the TURBINE carrier are presented in Figure 5. The results are similar to the STANDARD carrier where both oxygen and hydrocarbon are present, albeit in differing amounts. The first transformation observed occurs at 300°C and reaches a 45-percent reduction of NO_2 at 400°C in 316 stainless steel.

4. Presence of Water

The results reported above were obtained dry (i.e., 0-percent H_2O). To assess the effect of water, trials were also conducted with the water concentrations listed in Table 1, 14 percent H_2O for the STANDARD carriers, and 5 percent H_2O for the TURBINE carrier. The presence of water had no significant impact on reactivity for the STANDARD carriers in 316 stainless steel except for the case where both oxygen (5 percent) and hydrocarbons (500 ppm C_3H_6) are present. Here, the presence of water substantially increased the reactivity (Figure 6), from 20-percent to 85-percent reduction of NO_2 at 400°C. The impact of water in the 316 stainless steel on the TURBINE carrier, which has a higher oxygen (14 percent) and lower hydrocarbon content ($\sim$ 80 ppm), was not significant. In quartz, the water had no impact. The quartz was virtually passive for all carriers tested.

5. Probe Materials

In addition to the 316 stainless steel, various metallic materials were tested to determine if available alternatives to quartz would suppress the reduction of NO_2 at elevated temperatures. Both nickel and inconel tubes were tested, with negative results (Figure 7). Both materials exhibited substantially higher reactivity than the 316 stainless steel.

a) 316 Stainless Steel Probe
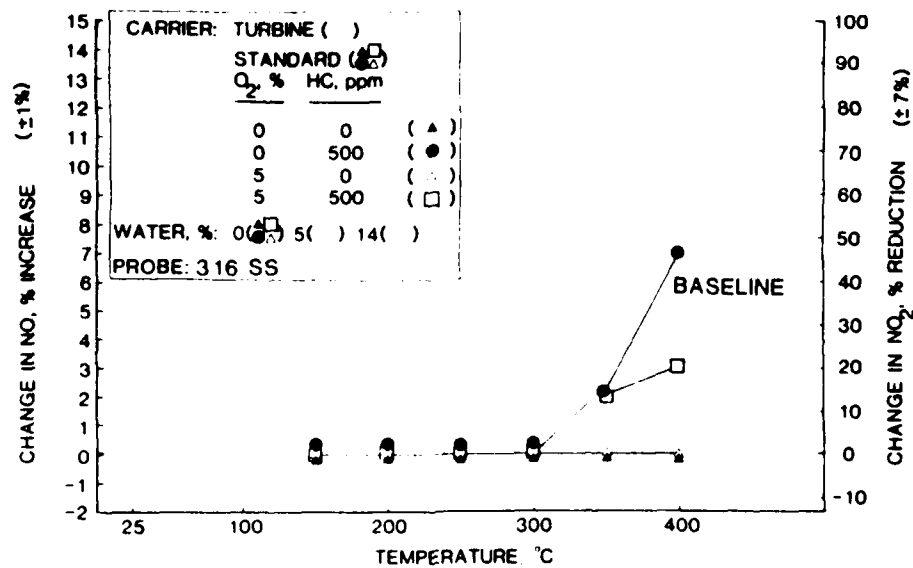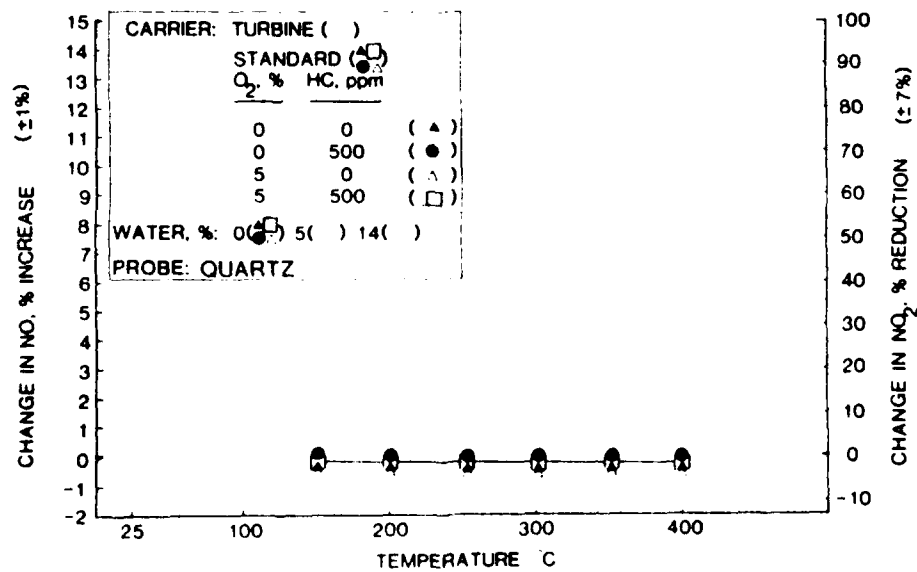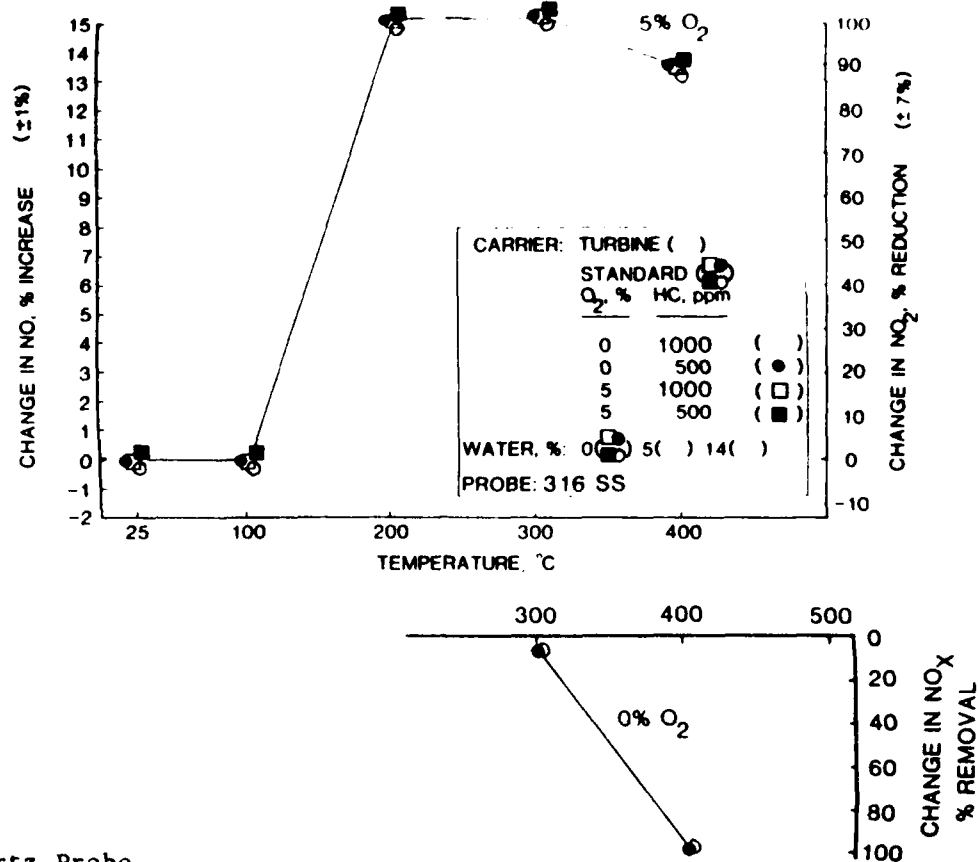

b) Quartz Probe

Figure 3. Effect of Carrier Composition

a) 316 Stainless Steel Probe
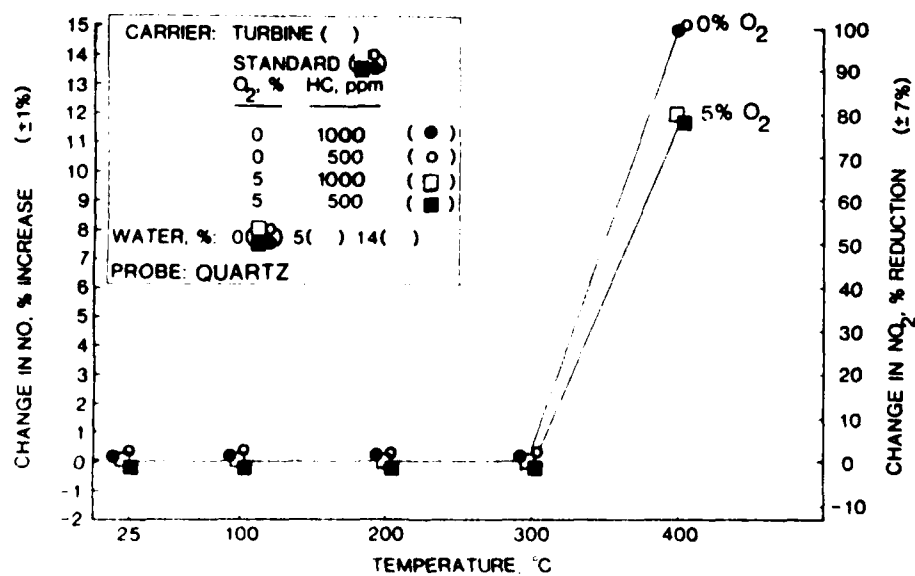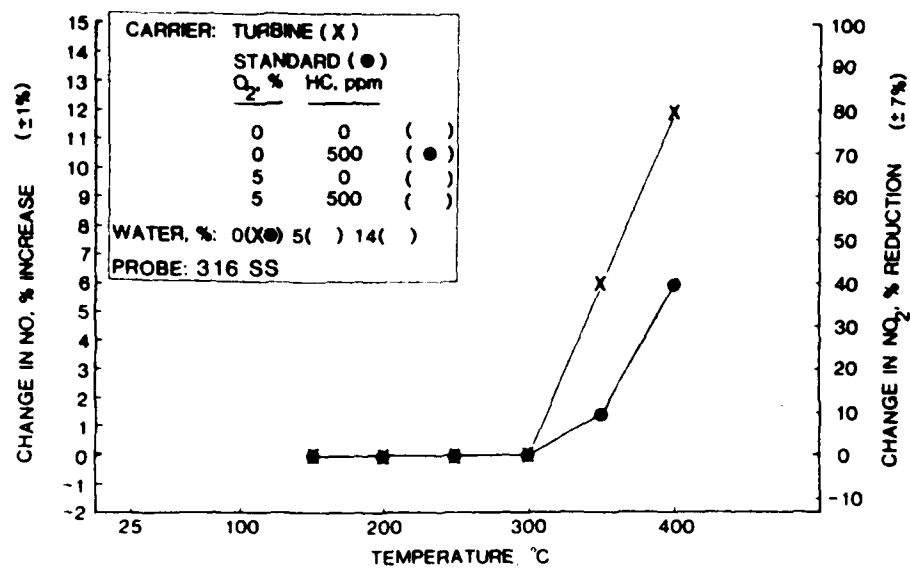

b) Quartz Probe

Figure 4.   Earlier Results (Reference 4)

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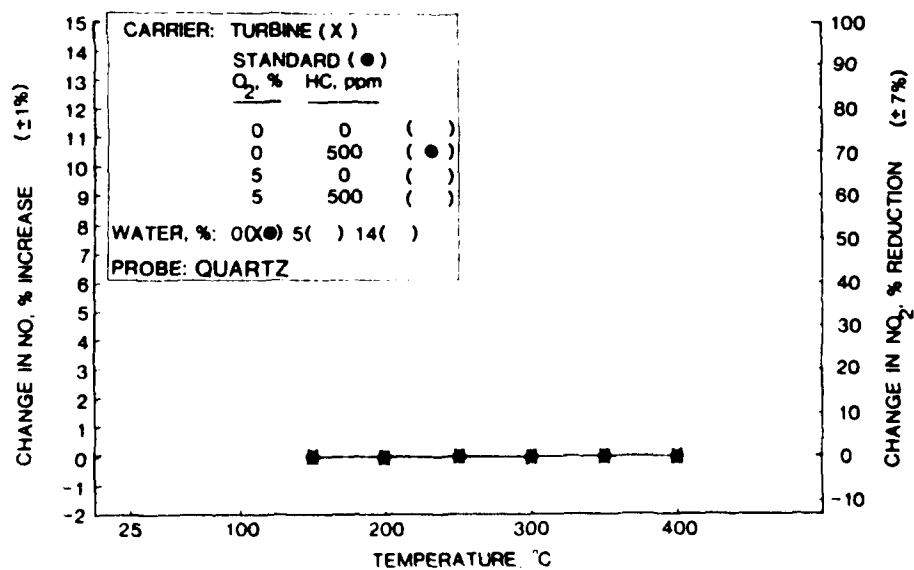a) 316 Stainless Steel Probe

b) Quartz Probe
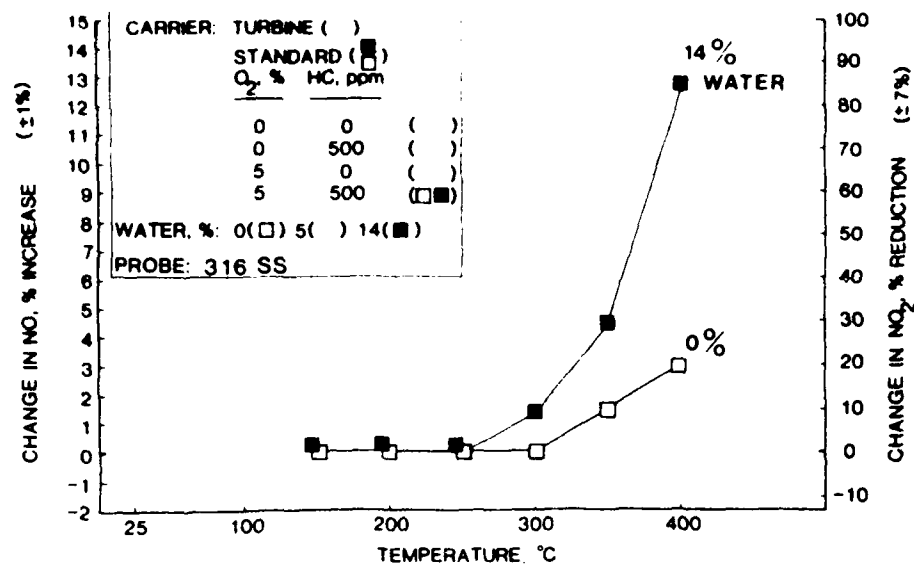

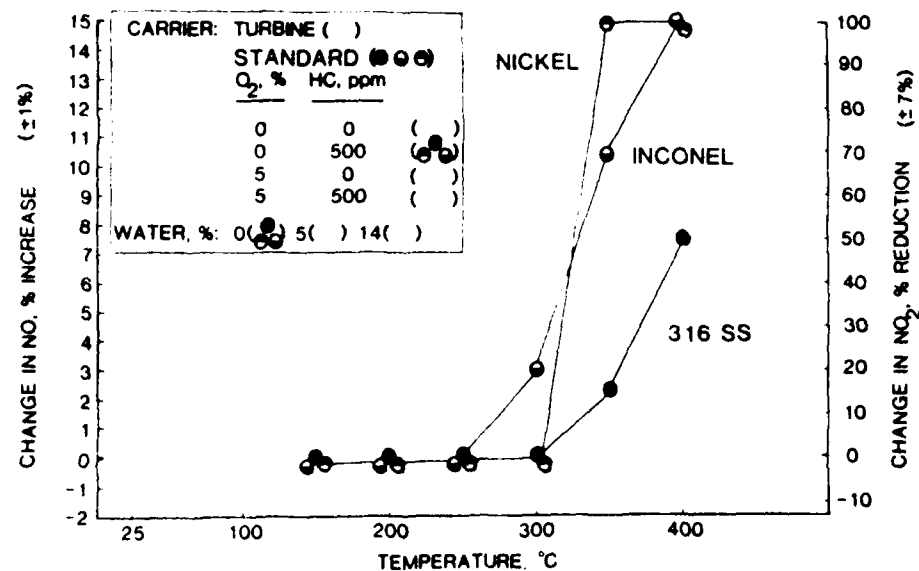Figure 5. TURBINE Carrier

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Figure 6.   Effect of Water

Figure 7.   Effect of Various Materials

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SECTION IV

CONCLUSIONS

NO_x is conserved in 316 stainless steel and quartz tubes up to 400°C. Above 400°C, NO_x can be destroyed.

The ratio of NO_2/NO is conserved up to 300°C in 316 stainless steel and 400°C in quartz. The present results were not changed appreciably by the presence or absence of water with one notable exception. In the stainless steel, the reactivity of the probe (reduction of NO_2 to NO) was significantly increased above 300°C (20-to 85-percent at 400°C) when both oxygen and hydrocarbons were present in the STANDARD CARRIER.

Stainless steel is more rugged than quartz and, as a result, more commonly used as a sampling probe material. The exploration of alternative metallic tube materials, such as nickel and inconel, was not successful in identifying a durable tube material that was less reactive than 316 SS. Both nickel and inconel were more reactive.

Based on the results of this study, quartz is clearly the most desirable material to use for sampling at elevated temperatures. Quartz was inert to all the sample compositions and sample temperatures explored in the present experiment. The one practical exception to the use of quartz is the vulnerability to breakage. Stainless steel tubes with quartz glass linings, available commercially, represent a reasonable solution where sample integrity is a major objective and reasonable handling of the probe can be maintained.

Should quartz or quartz-lined stainless steel not be an option, then type 316 stainless steel is a reasonable alternative. However, if stainless steel is used at temperatures exceeding 200°C, the tube should be water-cooled to ensure maintenance of sample integrity. Care must be excercised to cool the tube with hot water (> 60°C) to ensure that water in the combustion products does not condense.

REFERENCES

1. Benson, R.C., Samuelsen, G.S., and Peck, R.E., "Oxides of Nitrogen Transformations While Sampling Combustion Products Containing Carbon Monoxide," WSS/CI 76-11, 1976 Spring Meeting of the Western States Section, The Combustion Institute, Salt Lake City, 1976.

2. Benson, R.C., and Samuelsen, G.S., "Oxides of Nitrogen Transformation While Sampling Combustion Products Containing Carbon Monoxide, Hydrogen, and Hydrocarbons," WSS/CI 77-7, Spring Meeting of the Western States Section, The Combustion Institute, Seattle, 1977.

3. Samuelsen, G.S., and Harman, J.N., "Chemical Transformations of Nitrogen Oxides While Sampling Combustion Products," APCA Journal, Vol. 27, No. 7, July, p. 648, 1977.

4. Samuelsen, G.S., and Benson, R.C., "Chemical Transformations of Nitrogen Oxides While Sampling Combustion Products," Grosjean, D. (Ed.), Nitrogenous Air Pollutants -- Chemical and Biological Implications, Ann Arbor Science Publishers, Inc., Ann Arbor, p. 65, 1979.

5. Samuelsen, G.S., Hamberg, R.M., and Osborn, J.K., Composition and Concentration of Hydrocarbon Species Emitted from Gas Turbine Combustors, UCI Combustion Laboratory Report ARTR 78-3, Mechanical Engineering, University of California, Irvine, CA, 1978.

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