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TRANSFORMATION OF OXIDES OF NITROGEN COMPOSITION WHILE SAMPLING--ETC(U)

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TRANSFORMATION OF OXIDES OF NITROGEN COMPOSITION WHILE SAMPLING COMBUSTION PRODUCTS

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Abstract

Combustion products are regularly sampled to determine the concentration of the major products of combustion as well as the concentration of the pollutant species. Nitrogen oxides are especially susceptible to changes in concentration that may occur during transport from the sampling point to an instrument for quantitative analysis. The present study reviews the range of conditions over which nitrogen oxides are sampled in practice, and the variety of chemical transformations that may occur within probes and sample lines. In addition, experimental data are presented for chemical transformations that occur for mixtures common to stationary source monitoring, namely combustion products mixtures containing oxygen at temperatures ranging from 25°C to 400°C. Transformations in silica and stainless steel (304, 316, 321) tubing are evaluated. 316 and 321 stainless steel are observed to reduce nitrogen dioxide to nitric oxide at temperatures in excess of 300°C, and 304 stainless steel is observed to reduce nitrogen dioxide at temperatures in excess of 100°C. Silica is observed to be passive to chemical transformation over the temperature range evaluated. Total nitrogen oxides (NO_x) are conserved in all cases.

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Combustion products are regularly sampled to determine the concentration of the major products of combustion as well as the concentration of the pollutant species. Nitrogen oxides are especially susceptible to changes in concentration that may occur during transport from the sampling point to an instrument for quantitative analysis. The present study reviews the range of conditions over which nitrogen oxides are sampled in practice, and the variety of chemical transformations that may occur within probes and sample lines. In addition, experimental data are presented for chemical transformations that occur for mixtures

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common to stationary source monitoring, namely combustion products mixtures containing oxygen at temperatures ranging from 25°C to 400°C. Transformations in silica and stainless steel (304, 316, 321) tubing are evaluated. 316 and 321 stainless steel are observed to reduce nitrogen dioxide to nitric oxide at temperatures in excess of 300°C, and 304 stainless steel is observed to reduce nitrogen dioxide at temperatures in excess of 100°C. Silica is observed to be passive to chemical transformation over the temperature range evaluated. Total nitrogen oxides (NO_x) are conserved in all cases.

Introduction

The exhaust gas composition from anthropogenic sources such as spark-ignited reciprocating automobile engines, compression ignited diesel engines, package and industrial boilers, steam generating power plants, and gas turbine engines is measured to characterize system efficiency and pollutant emission levels. Measurement of the gaseous product composition emitted from a combustion source generally proceeds by extracting a sample for subsequent quantitative analysis. A typical sampling train is illustrated schematically in Figure 1. In order to maintain sample integrity, the sampling system must be evaluated to ensure that the analytical instrumentation receives a sample that truly represents the concentrations existing at the sampling point. Potential sample transformations should be minimized by careful selection of materials contacting sample gases in the physical probe used for sample removal and in the line used to transport the sample to instrumentation.

Of all the significant products of combustion, nitrogen oxides (NO_x) are especially susceptible to chemical transformation. The variety of combustion sources from which nitrogen oxides are emitted is presented in Table I. Shown are the broad ranges of effluent concentrations, sampling temperatures, and mixture ratios that may be encountered in operating systems.

Emission standards from combustion sources for nitrogen oxides are currently proposed or promulgated by the Environmental Protection Agency (EPA) in terms of total nitrogen oxides, NO_x[1-5].

As a result, emission factors are determined and compiled for mobile sources (*e.g.* the automobile) and stationary sources (*e.g.* power plants) in terms of total nitrogen oxide (NO_x). Current emissions inventories do not differentiate between the species of primary interest in the nitrogen oxides family, nitric oxide (NO) and nitrogen dioxide (NO_2). Yet the ratio of emissions of nitric oxide (NO) to nitrogen dioxide (NO_2) from combustion sources is of special interest for a number of applications. For example:

(1) The local air quality impact of nitrogen dioxide (NO_2) from major line sources requires knowledge of the amount of nitrogen dioxide (NO_2) emitted as a primary pollutant.

(2) Modeling the visibility of plumes from major power plants requires knowledge of the amount of nitrogen dioxide (NO_2) and nitric oxide (NO) emitted as primary pollutants.[6]

(3) The input to regional oxidant models requires a spatial and temporal geocoded emissions inventory of nitric oxide (NO) and nitrogen dioxide (NO_2) emission from mobile and stationary source operation.

(4) Flame probing in combustion research is conducted to identify mechanisms responsible for the formation of nitrogen oxides. Measurement of the ratio, NO/NO_2, is important to the determination of the chemistry acting.

Sampling Conditions

The sampling of combustion products from practical devices (utility boilers, package boilers, diesel engines, gas turbine engines, internal combustion engines), experimental devices (gas turbine combustors, combustion tunnels, stirred reactors), and directly from flames is conducted for a variety of reasons including enforcement, combustion characterization, pollutant formation studies, and efficiency optimization. Sampling is conducted at various locations within a given combustion system and over a wide range of temperatures and gas composition. In addition, the mixture sampled can be either oxidizing or reducing depending on the relative amount of oxidizing species (*e.g.* O_2) to reducing species (*e.g.* HC, CO) present at the sampling point.

Table I presents a summary of the typical sampling conditions encountered when measuring NO_x concentrations from combustion sources. In general, the sampling conditions may be classified into three major groups according to the temperature at which the sample is extracted:

moderate	25°C - 600°C
high	600°C - 1200°C
very high	1200°C - 2500°C

Moderate temperature probing (25-600°C) is the most frequently encountered. Flue and exhaust gas sampling from stationary and mobile sources occurs in the moderate temperature range. Examples include source sampling of effluents from utility boilers, package boilers, residential furnaces, diesel engines, gas turbine engines, and automobile engines.

High temperature probing is experienced in combustion research, especially in studies of secondary (post flame) combustion processes. Care is required to ensure that the reactions are terminated immediately upon extraction of the sample. Aerodynamic quenching (rapid cooling by immediate expansion of the hot gases through a choked orifice) is a common technique used to quench the reactions and freeze the species concentration.

• *Very high* temperature probing is common in flame research. Although flame research has been historically conducted in laboratory systems (premixed flames, diffusion flames, shock tubes, stirred reactors and plug flow reactors), combustion zones in practical combustion systems are now being probed as well.[7,8] Immediate and substantial cooling upon sample extraction is critical to ensure that the active reactions are quenched.

This paper addresses mechanical probing, namely sampling wherein a sample is extracted by a probe and conveyed to an instrument for analysis through a sample line. Excluded from consideration here are molecular beam and optical sampling methods. A review of the transformation reactions that may occur over the broad range of conditions represented by Table I is first presented. Second, experimental evidence of chemical transformation of nitrogen oxides is presented for the condition of oxygen containing atmospheres at moderate temperatures.

Chemical Transformation

Various sources of information are available to assist the practitioner in the design of sampling systems for the measurement of nitrogen oxides. The recognition that chemical transformation of nitrogen oxides can occur while sampling combustion products has prompted (1) a number of investigations that have explored specialized sampling conditions,[9-12] and (2) a few general reviews of the problems associated with sampling nitrogen oxides from combustion sources.[13-17] Additional information is available from studies conducted to evaluate converter materials for chemiluminescent oxides of nitrogen analyzers,[18-20] and from studies conducted to explore catalysis for potential use in the oxidation of CO in automobile exhaust by O_2 and NO.[21-23]

Types of Transformations

Chemical transformation of nitrogen oxides may be of three general types:

OXIDATION:	$NO \rightarrow NO_2$	NO_x conserved
REDUCTION:	$NO_2 \rightarrow NO$	NO_x conserved
REMOVAL:	$NO, NO_2 \rightarrow N_2$	NO_x not conserved

NO oxidation and NO_2 reduction reactions change the ratio of NO_2/NO without changing the total concentration of NO_x. (The oxidation of NO does produce a species, NO_2, that is more susceptible to removal by adsorption or absorption). The third transformation type, removal, acts to decrease the total NO_x concentration. Summaries of the transformation reactions that may be active in the sampling of combustion products are presented in Tables II, III, and IV for homogeneous, heterogeneous, and catalytic reactions respectively. (Although catalytic reactions may be either homogeneous or heterogeneous they are purposefully distinguished here as a separate subset.)

Homogeneous Reactions

NO Oxidation. The dominant gas phase oxidation reaction of NO is the termolecular combination with molecular oxygen to form nitrogen dioxide NO_2:

$$2NO + O_2 \rightarrow 2NO_2 \quad (1)$$

The reaction is important in the moderate temperature range from 25°C to 600°C. The rate of oxidation depends upon the concentration of O_2, NO, and NO_2, and decreases with increasing temperature.

NO_2 Reduction. The reverse of reaction (1)

$$2NO_2 \rightarrow 2NO + O_2 \quad (2)$$

becomes important as temperature increases. The temperature, then, is important in determining which reaction (1 or 2) is dominant. Although a kinetic analysis is required to determine the relative importance of the two reactions as a function of temperature, an equilibrium analysis is effective in describing the potential competition that can occur. For example, results of an equilibrium calculation are presented in Figure 2 as a function of temperature for a range of oxygen containing atmospheres (balance nitrogen). The initial nitrogen oxides concentration (500 ppm NO, 75 ppm NO_2) used for the calculations represents concentrations typical of those emitted from operating systems. The equilibrium predictions indicate that substantial changes in NO and NO_2 concentrations can occur given sufficient time. At temperatures below 200°C no change occurs unless oxygen is present. When oxygen is present, the NO is oxidized to NO_2

at low temperatures. At temperatures above 200°C, the equilibrium begins to shift to NO. The reduction of NO_2 to NO approaches completion at temperatures exceeding 600°C. The effect of oxygen on the percent transformed at 600°C is demonstrated by the detailed insert.

Whether chemical transformation, in fact, occurs via reactions (1) or (2) depends upon the rate of the two reactions at the temperatures of interest, the concentration of the reactant species, and the residence time. Uncatalyzed, reaction (1) does not advance sufficiently for typical sampling times (~ 10 sec) and representative reactant species concentration to significantly affect the NO_2/NO ratio. For example, at 500ppm NO, 75ppm NO_2, 5% O_2, balance nitrogen, the rate of NO_2 formation is 0.133ppm/sec at 100°C. At 400°C, the rate falls to 0.014ppm/sec. Even for levels of NO initially at 5000ppm, less than 3% of the NO will be oxidized to NO_2 after 10 seconds.[24] Unless catalyzed, reaction (2) is also too slow at moderate temperatures, relative to typical sampling times (~ 10 sec) to be important. For example, at 500ppm NO, 75ppm NO_2, 5% O_2, balance nitrogen, the rate of NO_2 reduction is 6.25×10^{-9} ppm/sec at 100°C and 6.33×10^{-2} ppm/sec at 400°C. At higher temperatures, however, the rate of reduction of the uncatalyzed reaction may be appreciable. For example, the rate of NO_2 reduction at 600°C via reaction (2) is 6.32ppm/sec and at 800°C increases to 112ppm/sec.[24]

The third homogeneous reaction presented in Table II,

$$NO_2 + O \rightarrow NO + O_2 \quad (3)$$

has been identified as potentially active when sampling in the very high temperature range (1200°C to 2500°C). Relatively long residence times and high concentrations of O-atoms are required for the concentration of NO_2 to be significantly reduced.[12]

NO_x Removal. Meyerson has demonstrated the homogeneous gas-phase removal of NO in the presence of hydrocarbons. Reduction of NO depends in part on maintenance of elevated temperatures (900°C to 1400°C) and careful control of oxygen to minimize the preferential oxidation of hydrocarbon species with oxygen.[25]

Heterogeneous Reactions

NO Oxidation. Allen has suggested that reaction (5) may explain the high concentrations of NO_2 observed by various investigators while sampling from flame zones (very high temperatures). The probe acts as a third body in promoting the radical relaxation of O-atoms with NO.[12] Other radical recombination reactions may participate as well.[26] If the radical species are not immediately quenched by the aerodynamic expansion, reaction (3) may dominate to yield a net reduction of NO_2 to NO.[12]

NO_2 Reduction. NO_2 reduction mechanisms have been the subject of numerous studies that address converter design for chemiluminescent NO-NO_x analyzers.[13-15] The dominant heterogeneous reactions investigated involve the reduction of NO_2 at the surface due to reactions with metals (*e.g.* vanadium, tungsten, manganese, molybdenum, and stainless steel) and carbon. The reactions are temperature sensitive and require temperatures in excess of 300°C to significantly advance the reduction of NO_2.[18-20] Carbon particulates formed in combustion processes can also participate in the chemical transformation of nitrogen oxides during sample transport. Heterogeneous reactions involving carbon particulates deposited on the walls of sample probes and sample lines can reduce NO_2 to NO in both overall reducing and overall oxidizing atmospheres.[15,26]

NO_x Removal. Nitrogen oxides may be removed by heterogeneous reactions at the wall of sampling materials. A dominant heterogeneous NO_x removal reaction is wall absorption or adsorption of NO_2. This is common with stainless steel, mild steel, and many metals.[13-16]

White and Beddows, among others, have found glass to be passive to the absorption of nitrogen dioxide (NO_2) at ambient temperatures.[27] TFE Teflon has also been evaluated in various studies with conflicting results. White and Beddows[27] found TFE Teflon to be passive at ambient temperature to NO_2 absorption whereas Trowell[28] and Healy and Urone[29] have observed strong absorption of NO_2 by TFE Teflon. The fact that conventional NO_2 permeation tubes are fabricated from FEP or TFE Teflon, and rely for function on the solubility of nitrogen oxides in the polymer lattice, indicate that these materials are not totally passive. The passivity of the TFE Teflon likely depends on the concentration of NO_2 and the total pressure of the sample.

Absorption in water condensate by reaction (9) is a principal removal mechanism for NO_2. Water is a major product of combustion and may condense on the walls of the probe and sampling lines if the probe and lines are not heated above the dew point. Nitrogen dioxide (NO_2) is water soluble and will be removed by absorption if caution is not exercised to maintain the sample above the dew point temperature in probes and sample lines leading to the analytical instrumentation.[13,16,30] Water is purposefully removed in many situations to protect analytical instrumentation, remove a potentially interfering gas, and/or measure the composition of a dry sample. In such cases, special care is required to ensure that NO_2 is not also removed.[15,17]

Given sufficient time, other heterogeneous reactions may remove NO_x. A two-step mechanism is suggested by Brietenbach and Shelef that leads to the removal of NO via the oxidation of surface carbon by gaseous oxygen to carbon monoxide, and the subsequent oxidation of the carbon monoxide by nitric oxide to form N_2 and CO_2.[20] The NO may be reduced directly by carbon as indicated by reaction (11). Both reactions (10) and (11) are of special concern in carbon converters used for chemiluminescent analyzers, and suggest that caution must be exercised in setting and maintaining carbon converter temperatures.

Catalytic Reactions

<u>NO Oxidation</u>. Catalysts can promote the oxidation of NO to NO_2. Halstead reports that oxidized or heat treated surfaces

can be especially active in oxidizing NO to NO_2.[13] Additional studies are required to determine the extent of catalytic oxidation of NO for sample times (~ 10 sec) and materials used in sampling nitrogen oxides from combustion effluents.

NO_2 Reduction. In parallel with the NO-NO_x chemiluminescent converter studies in which various heterogeneous paths for the reduction of NO_2 to NO have been evaluated, catalytic reduction reactions of NO_2 have also been studied.[18,19,20,27,31] Catalytic materials evaluated include stainless steel, gold wool, and quartz. The overall reaction generally regarded as operative in the catalytic reduction of NO_2 is:

$$NO_2 \xrightarrow{\text{catalytic}} NO + \tfrac{1}{2}O_2 \qquad (12)$$

Reaction (12) may advance significantly in times typical of sampling (~ 10 sec). The effect of temperature on the dissocation of NO_2 may be implied from Figure 2. Dissociation begins at temperatures exceeding 100°C and is effectively complete at temperatures in excess of 600°C. The oxygen content of the sample will determine the temperature required for complete (> 98%) conversion.

NO_x Removal. The catalytic reduction of NO by CO has been explored by various investigators for possible application to automobile exhaust control.[21-23] Reduction reactions involving hydrogen and hydrocarbons can occur in parallel with the CO attack on NO, and have also been the subject of recent inquiries.[32,34]

With respect to sampling combustion products, the work of Halstead is the most definitive statement with respect to the chemical transformation of nitrogen oxides to expect when sampling combustion products containing carbon monoxide. Halstead sampled combustion products from a "Tunnel Mixing Burner" operating on natural gas and air. Two probe materials (stainless steel 210 cm long by 6 mm i.d., and silica tubing, 210 cm long x 4 mm i.d.) were evaluated for lean and rich burn conditions. The temperature at the probe inlet, measured with suction pyrometry, varied between 800 and 1700°C. The temperature of the sample at the outlet was near ambient. The residence time was estimated to be 4 seconds. Under the lean fire conditions, Halstead found no change in NO_x concentration for either the stainless steel or silica tubing. Changes were observed for rich fire with the stainless steel probe. In particular, the nitrogen oxides (NO_x) concentration decreased in excess of 90 percent. No effect was observed for the silica.[9] Although the results suggest that important chemical transformation occurs when sampling fuel rich combustion products with stainless steel, important questions remain unanswered. For example, the data are not sufficient to establish the active reactions. Halstead suggests that reaction (14) may be the key to the reduction.[9] However, the extent to which the various reducing species (*e.g.* carbon monoxide, hydrogen, and hydrocarbons) participate in the reduction reactions cannot be assessed. In addition, the varying temperature along the probe length does not allow determination of the temperature at which the reduction reactions are active.

Experiment

A variety of reactions may participate in the chemical transformation of nitrogen oxides while sampling combustion products. The assessment of transformations that may occur under conditions experienced when sampling combustion products requires experiments that are specifically designed to identify (1) the chemical transformations, if any, that occur, (2) the extent to which they occur during typical sampling times, and (3) the conditions (*e.g.* sample temperature, sample composition, sample line material) for which they occur.

The present study includes an experiment designed to assess transformation reactions for a specific class of practical combustion devices that operate air-rich--namely boilers, diesel engines, and gas turbine engines. Results are presented for the moderate temperature range typical of exhaust or flue gas sampling. A schematic of the experimental system is shown in Figure 3. The overall design reflects the need to simulate the actual conditions experienced in sampling gaseous combustion products from the variety of sources shown in Table I. Test parameters include carrier gas composition, concentration, and composition of the dopant gases, pre-probe carrier gas temperature, post-probe carrier gas temperature, and probe material.

For the present study, carrier gas is selected from one of three prepared sources of 0, 1, and 5% O_2, 12% CO_2, balance N_2. The carrier gas flow, 4 liters/minutes, is doped with NO and NO_2 metered from high concentration source cylinders by means of porous sintered metal flow restrictors. The carrier gas enters a silica preheat oven to raise the gas temperature to the probe test temperature. From this point, the doped carrier gas enters the sample probe test section.

The NO and NO_2 input levels are chosen to be 500 ppm NO and 75 ppm NO_2 respectively. These levels simulate NO levels which are typically encountered and NO_2 levels which are representative of those generally thought to exist in combustion source effluents. Sample probe materials evaluated include 304, 316, and 321 stainless steel and silica glass. The length of each sample probe is arbitrarily chosen to be 2 meters. The residence time of the doped carrier gas in the sample probe test section is approximately 1 second for the 4 liters/minute flow rate and 2 meter sample probe length.

The gas temperature within the sample probe is incrementally increased from 25°C to 400°C. Temperatures of the gas stream (T_2 and T_3) are measured with insulated platinum resistance thermometers centered in the probe bore at the inlet and outlet of the sample probe. The oven temperature is also recorded by a thermocouple located adjacent to the outer diameter of the sample probe.

Gas composition is determined before and after the probe to assess the extent of NO and NO_2 transformation within the 2 meter sample probe segment. Sample lines leading from points 2 and 3 (Figure 3) are short, equal-distant, and made of 1/4 inch diameter

TFE Teflon. Screening tests using varying lengths of TFE Teflon were conducted for the current study to assure that NO_2 absorption was not a significant factor in the present experiment. However, a systematic evaluation was not conducted and is needed to explain the reported differences in NO_2 absorption on TFE Teflon.[27-29]

Analysis of NO and NO_x is conducted with a Beckman Model 951H chemiluminescent oxides of nitrogen analyzer. NO_2 is determined by difference. The (carbon) converter efficiency is monitored by periodic tests using the methods outlined in the Federal Register.[3]

Results

The results are presented in Figures 4 and 5 for the silica and the three stainless steel sample probes respectively. The percent change of NO and NO_2 represent the percent change in concentration between sample points 2 and 3. The temperature shown is the gas temperature at sample points 2 and 3.

The results for silica are presented in Figure 4. No significant transformation occurs over the temperature range and the residence time studied. Evidence of NO oxidation, proportional to oxygen content, is discernible, however.

The results for 304 stainless steel are presented in Figure 5a. A significant transformation (reduction of NO_2 to NO) occurs at temperatures in excess of 100°C. Conversion of NO_2 to NO at elevated temperature by stainless steel is consistent with the results of a variety of studies (Table IV) in which stainless steel has been evaluated for use as the converter material in chemiluminescent nitrogen oxides analyzers. At temperatures below the catalytically active temperature of 200°C, no significant change is observed. The oxygen content of the mixture has an important impact on the conversion efficiency at the peak temperature evaluated (400°C).

The results for the 316 stainless steel, presented in Figure 5b, indicate a higher temperature for catalytic reduction of NO_2 in comparison to 304 stainless steel. Chemical transformation of nitrogen oxides is negligible for temperatures of 300°C or lower. At 400°C, however, dissociation is nearly 100% complete. The oxygen content of the mixture has a modest impact on the conversion efficiency at the peak temperature evaluated (400°C).

The results for the 321 stainless steel, presented in Figure 5c, show behavior similar to the 316 stainless steel.

The three stainless steels evaluated are similar in the composition of carbon, chromium, and nickel. As shown in Table V, however, 316 stainless steel has molybdenum added to improve corrosion resistance, and 321 stainless steel has titanium added to reduce carbide precipitation. In general, stainless steels have strong resistance to corrosion due to an oxidized layer on the surface. Reducing atmospheres can remove the film and change the passivity. It is likely then that probe history can impact the chemical transformation of nitrogen oxides. Some evidence of this effect has been reported in the literature,[15] but a full assessment has yet to be made.

Conclusions

Nitrogen oxides may undergo various chemical transformations between the sampling point and the instrument used for detection. The present study has reviewed reactions that may contribute to chemical transformation of nitrogen oxides for the three temperature ranges encountered in practice -- *moderate, high, very high* -- and has addressed experimentally chemical transformation, that can occur during moderate temperature combustion source sampling and analysis. In particular, chemical transformation of nitrogen oxides has been explored for those practical combustion devices that operate air-rich, namely boilers, diesel engines, and gas turbine engines.

The conclusions drawn are presented below under two categories: Specific (with respect to the present experiment) and General (with respect to actual source monitoring application). For the conditions explored,

Specific

- o NO_x is conserved in silica and 304, 316, and 321 stainless steel sample probes for the temperature range 25 to 400°C and a residence time of 1 second.
- o Reduction of NO_2 is observed in 316 and 321 stainless steel sample probes at temperatures exceeding 300°C. In 304 stainless steel sample probes, reduction is observed at temperatures exceeding 100°C.

- In silica probes, no significant chemical transformation of nitrogen oxides is observed.

<u>General</u>

- Chemical transformation in nitrogen oxides concentration while sampling combustion products should be expected under all conditions.
- Chemical transformation in nitrogen oxides concentrations are likely to occur when sampling combustion products in excess of 300°C using 316 and 321 stainless steel, and in excess of 100°C using 304 stainless steel sample probes.
- Chemical transformation in oxides of nitrogen concentration may be effectively prevented by (1) using only silica materials, and (2) exercising appropriate precaution in handling water in the sample.
- Previous NO_x, NO, and NO_2 data collected at moderate temperatures (25 to 600°C) with stainless steel must be used with caution.
- Additional information is needed to guide the selection of probe and sample line materials in order to minimize the occurrence of chemical transformation and to determine the extent of chemical transformation under the variety of sampling conditions experienced in practice.

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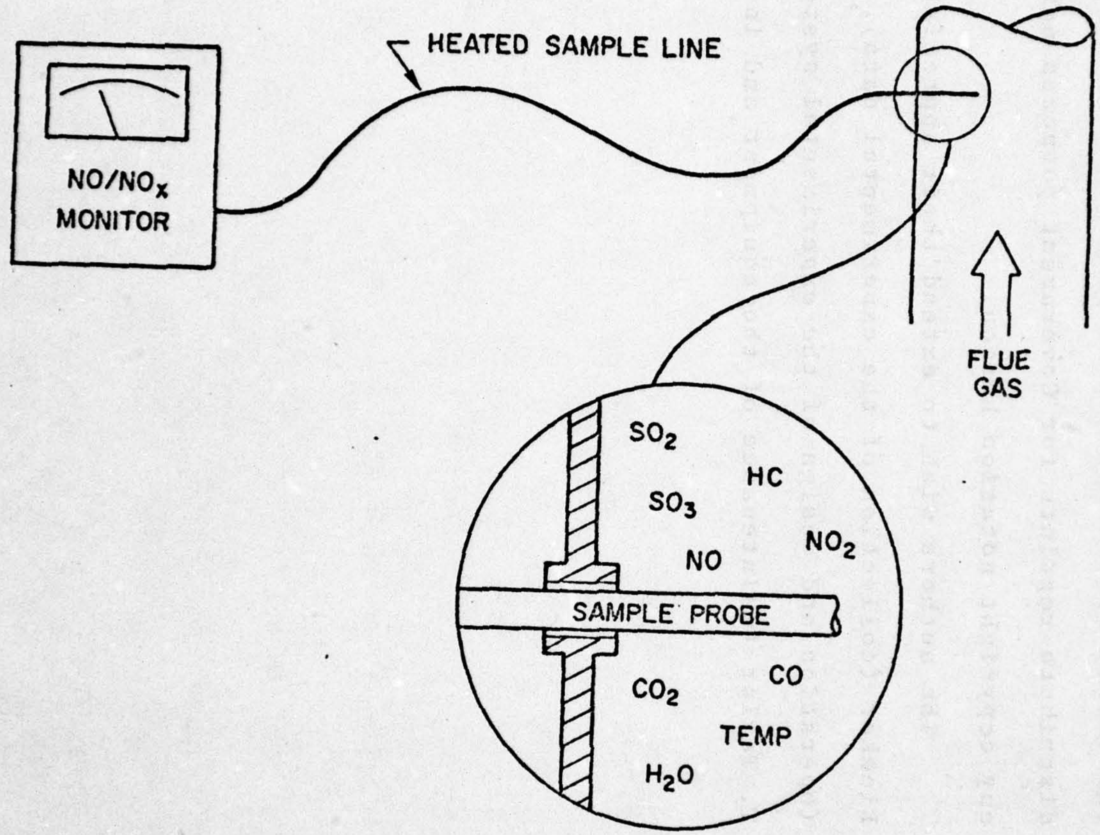

Figure 1 Schematic--Combustion Product Sampling for NO/NO_x

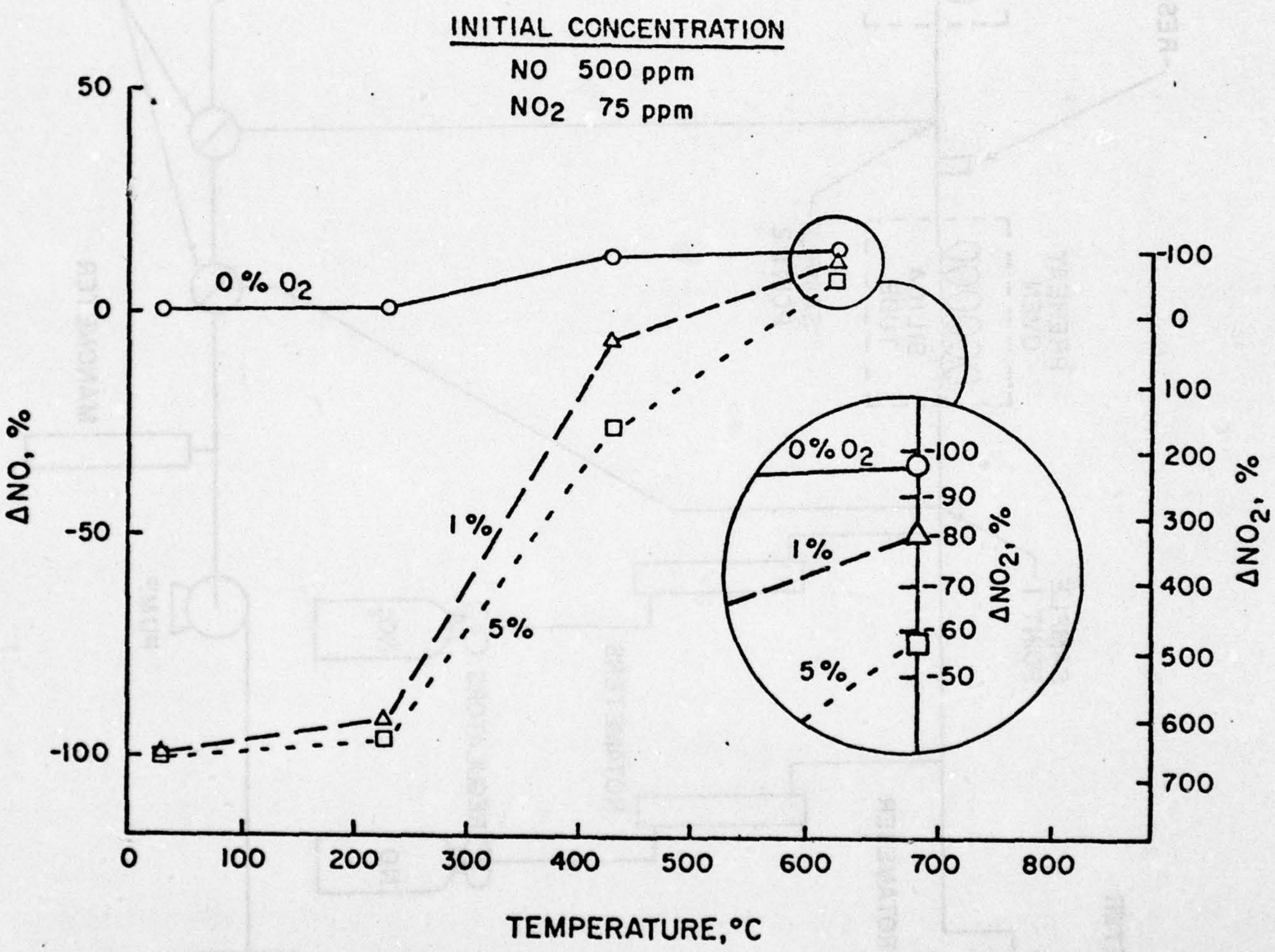

Figure 2 Predicted (Equilibrium) Change of NO and NO_2 Concentration as a function of Temperature at 0, 1, 5% O_2

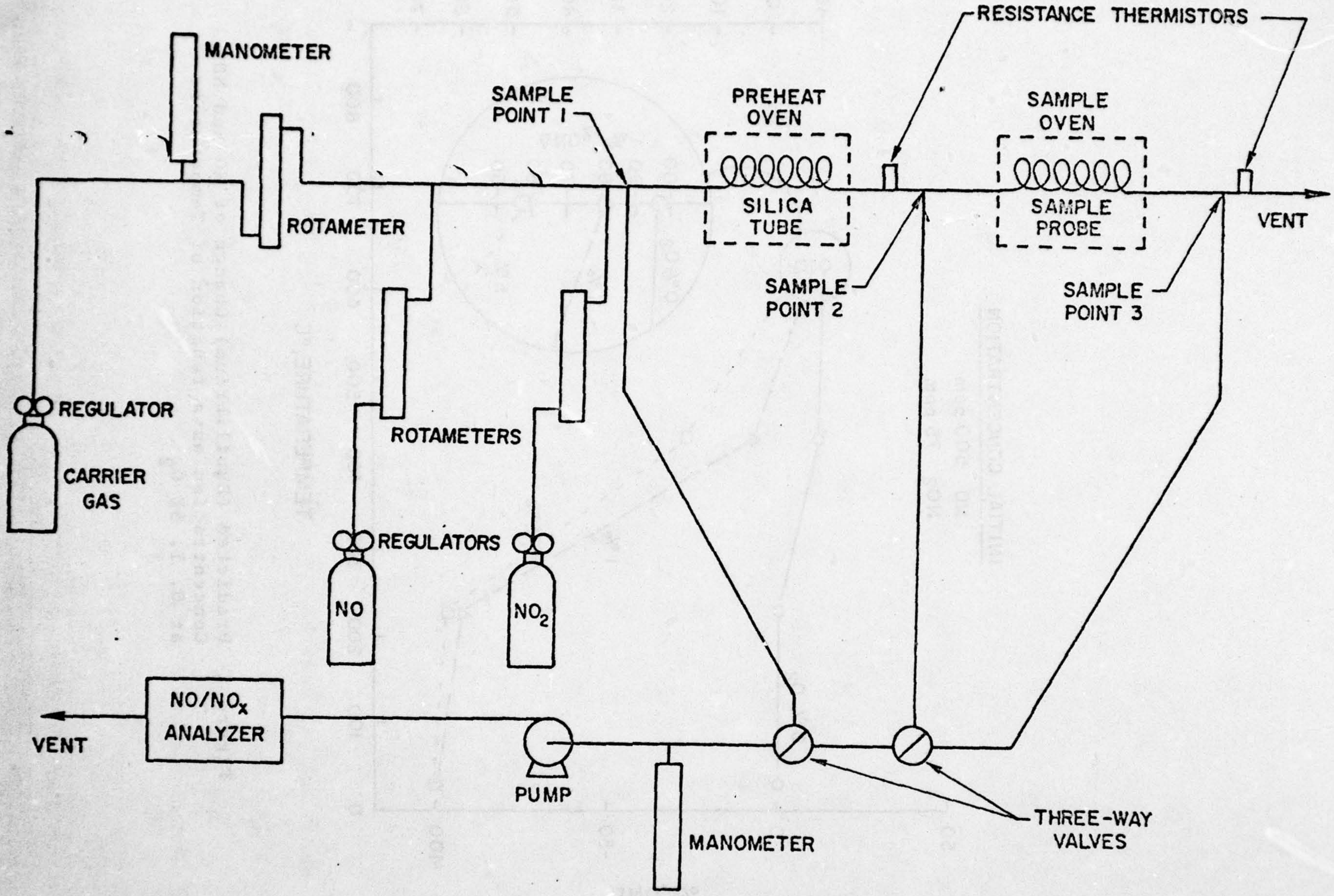

Figure 3 Schematic--Experimental System

Figure 4 Silica Test Probe

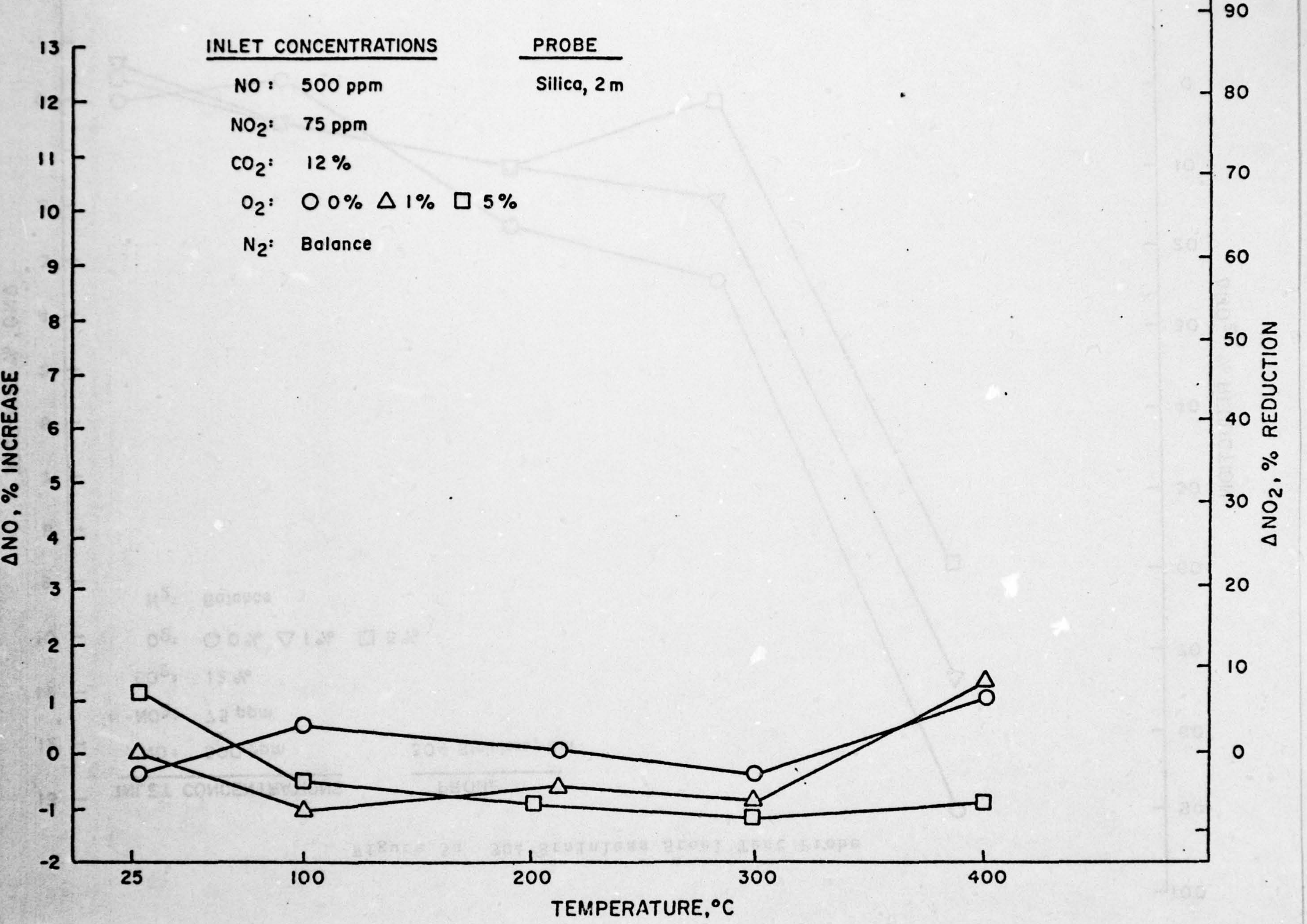

Figure 5a 304 Stainless Steel Test Probe

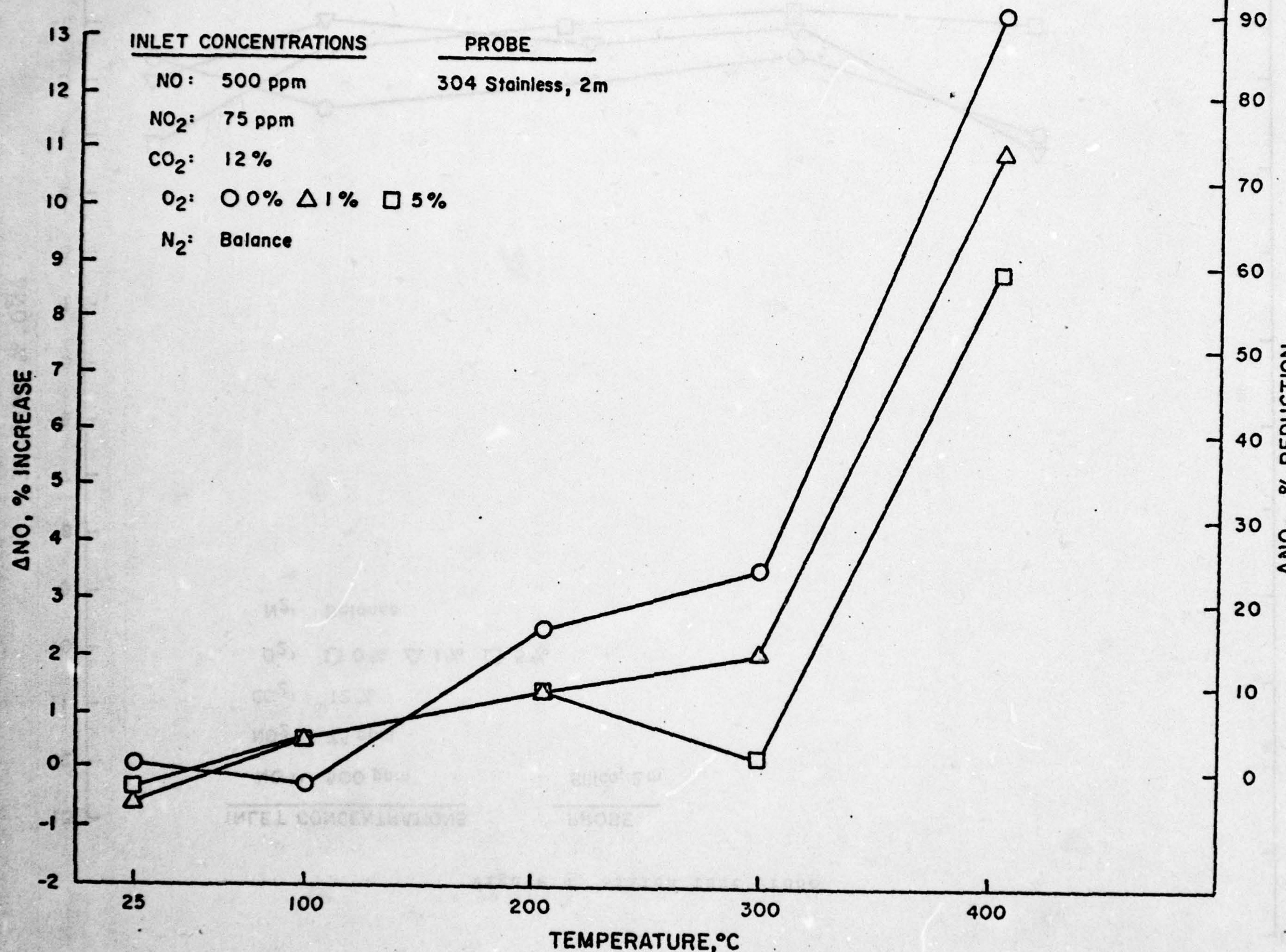

Figure 5b Stainless Steel Test Probe

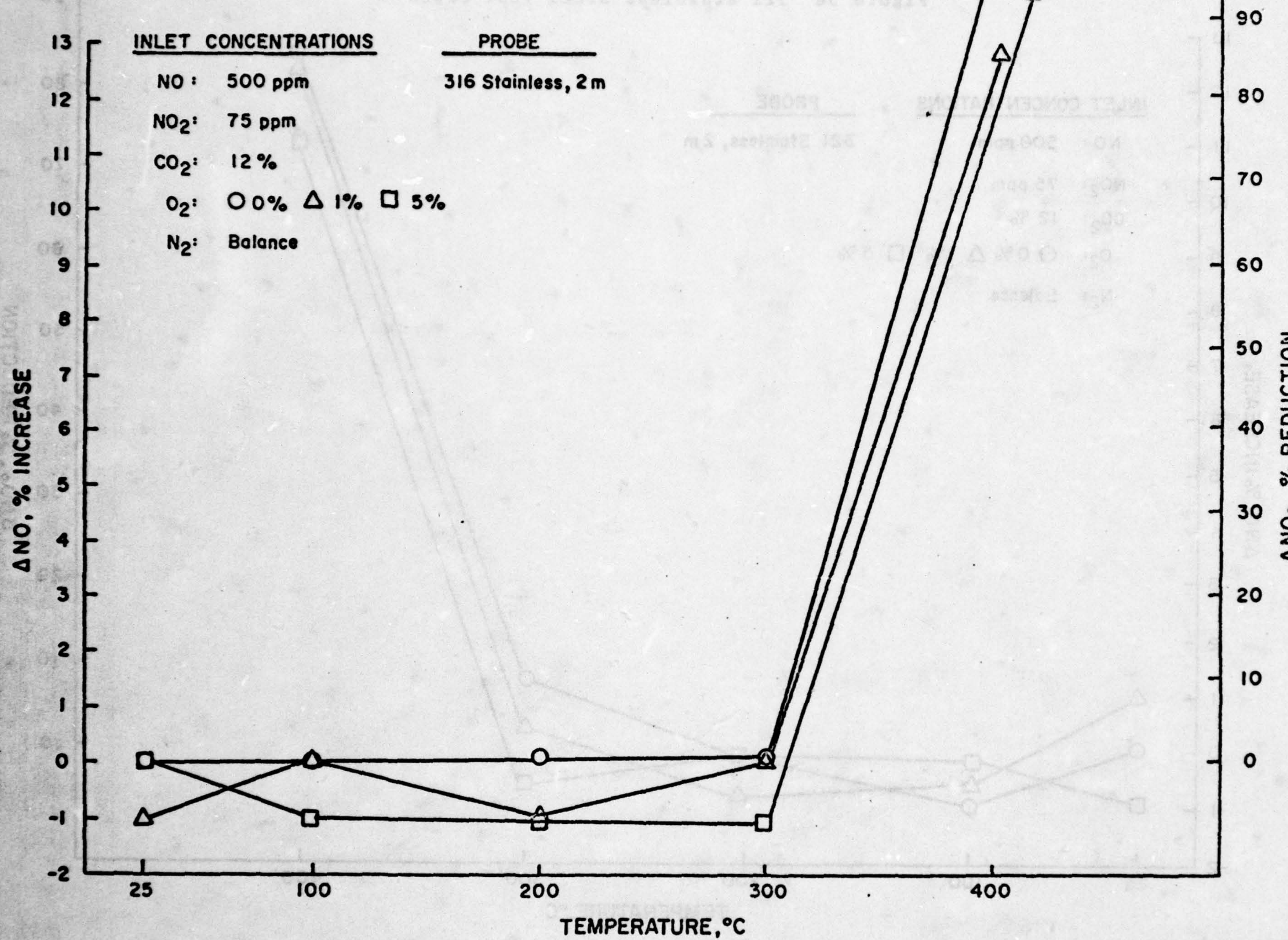

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Figure 5c 321 Stainless Steel Test Probe

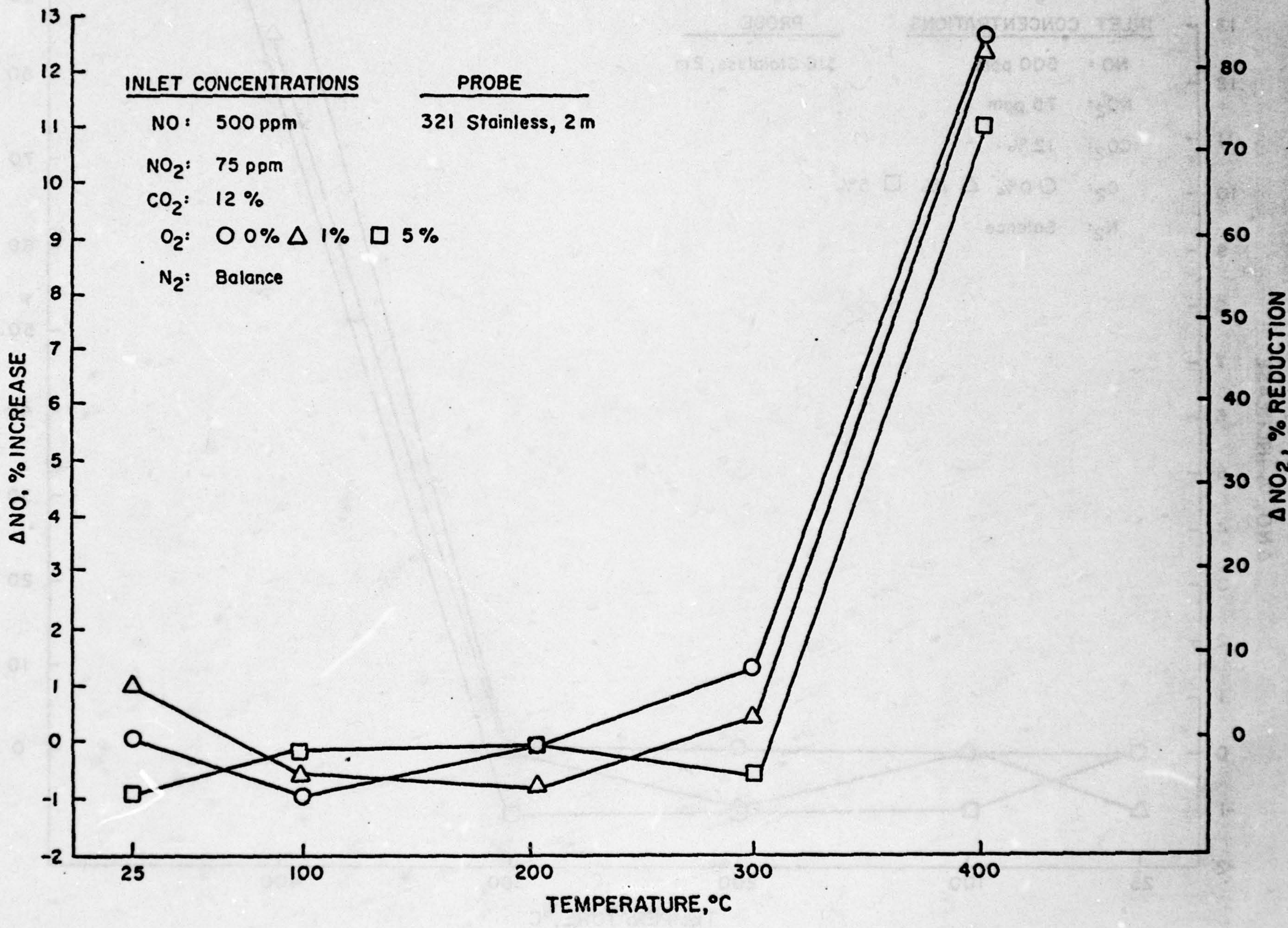

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Table I Sampling conditions for nitrogen oxides.

Source	Typical NO_x ppm	Sampling Point	Typical Sampling Environment: Temperature °C	Typical Sampling Environment: Atmosphere	References: Examples of NO_x probing	References: Prior Studies Relevant to Possible NO_x Transformations
Internal Combustion Engine	500-4000	Combustion Zone	1300-2400	Reducing	38, 39	--
	500-1000	Engine Exhaust	200-500	Reducing	3, 5	9
Diesel Engine	1000-7000	Combustion Zone	700-2500	Reducing and Oxidizing	40	--
	700-2500	Engine Exhaust	200-500	Oxidizing	4	9
Residential Oil Burners	20-100	Flue Gas	100-300	Oxidizing	41	9
Boilers	200-1000	Combustion Zone	100-1600	Reducing and Oxidizing	7, 8	10, 11, 12
	25-800	Flue Gas	100-300	Oxidizing	1, 42, 43	9
Gas Turbine	1000-8000	Combustion Zone	1300-2700	Reducing and Oxidizing	15	--
	25-200	Engine Exhaust	400-1500	Oxidizing	44, 45, 46, 47, 48	9, 15
Flame Research	10-8000	Within Flame	700-2500	Reducing and Oxidizing	49, 50, 51, 52, 53, 54	10, 11, 16

Table II Homogeneous reactions.

Transformation		Reaction	Reference[a] COMB	CONV
NO Oxidation	(1)	$2\ NO + O_2 \rightarrow 2\ NO_2$	9, 13	55
NO_2 Reduction	(2)	$2\ NO_2 \rightarrow 2\ NO + O_2$		19, 56
	(3)	$NO_2 + O \rightarrow NO + O_2$	12	
NO_x Removal	(4)[b]	$NO + CH \rightarrow HCO + N$	25	

[a]COMB: Combustion Related Study
CONV: Converter Related Study

[b]CH: Hydrocarbon

Table III Heterogeneous reaction.

Transformation		Reaction	COMB	CONV	OTHER
			Reference[a]		
NO Oxidation	(5)	$NO + O \xrightarrow{wall} NO_2$	12		
NO_2 Reduction	(6)	$NO_2 + metal \xrightarrow{wall}$ metal oxide + NO	27	20	
	(7)	$NO_2 + C \xrightarrow{wall} CO + NO$	26	20,57	
NO_x Removal	(8)	$NO_2 \xrightarrow{wall}$ absorbed adsorbed	9, 13, 16 27		28,29
	(9)	$NO_2 \xrightarrow{condensate}$ absorbed	16, 30		
	(10)	$C + \frac{1}{2} O_2 \xrightarrow{wall} CO$		20	
		$NO + CO \xrightarrow{catalytic} \frac{1}{2} N_2 + CO_2$			
	(11)	$NO + C \xrightarrow{wall} CO + \frac{1}{2} N_2$		20	

[a]COMB: Combustion Related Study
CONV: Converter Related Study

Table IV Catalytic reactions.

Transformations		Reactions	References[a] COMB	CONV	CAT
NO Oxidation	(12)	$NO + \frac{1}{2} O_2 \longrightarrow NO_2$	13		
NO_2 Reduction	(13)	$NO_2 \longrightarrow NO + \frac{1}{2} O_2$	14	18,19,20, 27,31	
NO_x Removal	(14)	$NO + CO \longrightarrow CO_2 + \frac{1}{2} N_2$	9,13		21,22, 23
	(15)	$5 H_2 + 2 NO \longrightarrow 2NH_3 + 2 H_2O$			32,33, 34

[a]COMB: Combustion Related Study
CONV: Converter Related Study
CAT: Catalyst Study

Table V Stainless steel composition.[a]

Specification	S.S. Type	Typical Weight Percent				
		Carbon	Chromium	Nickel	Molybdenum	Titanium
General[35]	304	0.08	18-20	8-12		
	316	0.08	16-18	10-14	2-3	
	321	0.08	17-19	9-12		0.40
Present Study[36,37]	304	0.05	18.12	8.64		
	316	0.004	17.60	12.48	2.72	
	321	0.065	17.75	10.78	0.30	0.47

[a] other elements present include manganese, phosphorus, sulfur, silica, copper