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Chemical Transformations of Nitrogen Oxides While Sampling Combustion Products

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The present study reviews the sampling environments and chemical transformations of nitrogen oxides that may occur within probes and sample lines while sampling combustion products. Experimental data are presented for NO_x transformations in silica and 316 stainless steel tubing when sampling simulated combustion products in the presence of oxygen, carbon monoxide, and hydrogen. A temperature range of 25° to 400°C is explored. In the absence of CO and H_2 , 316 stainless steel is observed to promote the reduction of nitrogen dioxide to nitric oxide at temperatures in excess of 300°C, and silica is found to be passive to chemical transformation. In the presence of CO, reduction of NO_2 to NO is observed in 316 stainless steel at temperatures in excess of 100°C, and reduction of NO_2 to NO in silica is observed at 400°C. In the presence of H_2 , NO_2 is reduced to NO in 316 stainless steel at 200°C and NO_x is removed at temperatures exceeding 200°C. In silica, the presence of H_2 promotes the reduction of NO_2 to NO at 300°C and the removal of NO_x above 300°C.

Measurement of the exhaust gas composition from anthropogenic sources such as automobile engines, diesel engines, utility and industrial boilers, furnaces, and gas turbine engines is required to evaluate system efficiency and pollutant emission levels. Measurement generally proceeds by extracting and transporting a sample to instrumenta-

tion for quantitative analysis. To obtain reliable data, it is necessary that the analytical instrumentation receive a sample that is chemically identical to the composition existing at the point of extraction.

Potential sample transformations may be minimized by careful selection of materials for the probe and sample line. However, careful selection requires data relevant to the application, and data are presently not plentiful for two products of combustion especially susceptible to chemical transformation, nitric oxide (NO) and nitrogen dioxide (NO_2). This paper summarizes the available information and presents results from an experiment designed to assess the conditions for which chemical transformation of nitrogen oxides occurs.

Types of Transformation

Chemical transformation of nitrogen oxides in probes and sample lines may be of three general types:

NO Oxidation: $\text{NO} \rightarrow \text{NO}_2$
 NO_x conserved

NO_2 Reduction: $\text{NO}_2 \rightarrow \text{NO}$
 NO_x conserved

NO_x Removal: $\text{NO}, \text{NO}_2 \rightarrow \text{N}_2$
 NO_x not conserved

An additional transformation path, formation, involves the oxidation of nitrogen containing species such as ammonia (NH_3). Because formation of NO_x in probes and sample lines is generally limited to specialized conditions (e.g. sample extraction from flue gases into which ammonia has been injected for NO_x control, or from flames into which nitrogen containing compounds have been injected to study fuel bound NO_x formation), formation reactions are not separately identified.

The potential significance of the transformation of nitrogen oxides rests on the use of the emissions data. For example, emission standards for nitrogen oxides are currently proposed or

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Table I. Sampling conditions for nitrogen oxides.

Source	Typical NO _x ppm	Sampling point	Typical sampling environment		Examples of NO _x probing	References
			Temperature °C	Atmosphere		Prior studies relevant to possible NO _x transformations
Internal combustion engine	500–4000 500–1000	Combustion zone Engine exhaust	1300–2400	Reducing	42, 43 3, 5	14
			200–500	Reducing		
Diesel engine	1000–7000 700–2500	Combustion zone Engine exhaust	700–2500	Reducing and Oxidizing	44 4	14
			200–500	Oxidizing		
Residential oil burners	20–100	Flue gas	100–300	Oxidizing	45	14
Boilers	200–1000 25–800	Combustion zone Flue gas	100–1600	Reducing and Oxidizing	7, 8 1, 46, 47	15, 16, 17 14
			100–300	Oxidizing		
Gas turbine	1000–8000 25–200	Combustion zone Engine exhaust	1300–2700	Reducing and Oxidizing	11 25, 48, 49, 50, 51	11, 14
			400–1500	Oxidizing		
Flame research	10–8000	Within flame	700–2500	Reducing and Oxidizing	52, 53, 54, 55, 56, 57	15, 16, 17

promulgated in terms of nitrogen oxides, NO_x.^{1–5} As a result, the enforcement of emission standards is not compromised by the occurrence of NO oxidation or NO₂ reduction reactions in the probe or sample line so long as total oxides of nitrogen are conserved. However, emissions data biased by NO_x removal reactions are unacceptable as the basis for any emissions standard, control strategy, or enforcement action.

In addition to conserving NO_x, the influence of NO oxidation and NO₂ reduction reactions in probes and sample lines warrants increased attention as well. For example:

1. Assessment of local air quality impact

The NO/NO₂ emission ratio is important in assessing local air quality impact from major sources. Ambiguity regarding the NO/NO₂ emission ratio from combustion sources presently precludes consideration of the impacts of NO and NO₂ emissions on areas in proximity to the source.

2. Assessment of plume visibility impact

The NO/NO₂ emission ratio is important in the prediction of plume visibility from power plants.⁶ The ambiguity regarding the NO/NO₂ emission ratio from power plants presently precludes a full assessment of air quality and plume visibility impact, and compromises attempts to validate visibility impact models.

3. Regional oxidant modeling

The prediction of local formation and removal rates for oxidant requires spatial and temporal emission inventories for both NO and NO₂. Ambiguity regarding the NO/NO₂ emission ratio from mobile and stationary sources

contributes to the limitations of regional oxidant models and compromises efforts to validate these models.

4. Flame studies

The local concentrations of both NO and NO₂ within flames are required to assess the chemical kinetic mechanisms responsible for the formation of NO_x. Questions attendant to transformation of NO and NO₂ in sample probes presently limit the utility of fundamental studies that address NO and NO₂ formation in combustion flows.

Sampling Conditions

Table I is a summary of the conditions typically encountered when measuring combustion product composition. Note the wide variation of temperature and species concentration. The temperatures encountered (at the point of sample extraction) divide into three general groups:

Temperature Group	Temperature Range
moderate	25°–600°C
high	600°–1200°C
very high	1200°–2500°C

Moderate temperature probing (25°–600°C) is the most frequently encountered. Examples include flue and exhaust gas sampling from stationary and mobile sources. *High* temperature probing is experienced in combustion research, especially in studies of secondary (post flame) combustion processes. *Very high* temperature probing is common in flame research. Although flame research has historically been 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}

The function of the sample probe is to extract and cool the sample to a final temperature. (For *high* and *very high* temperature probing, rapid expansion of the sample at the probe tip is employed to terminate active reactions.) The final temperature is typically controlled (150° to 200°C) to prevent condensation of water and hydrocarbons. The function of the sample line is to maintain the final temperature and transport the sample to the analytical instrumentation.

Chemical transformations of nitrogen oxides in the temperature range 25° to 600°C are of special interest since (1) moderate temperature probing (25° to 600°C) is the most frequently encountered, and (2) regardless of the temperature at the point of extraction, the sample will typically have an extended residence time (seconds) at the final temperature (150° to 200°C) while undergoing transport to the analytical instrumentation.

Available Information

A few general reviews of NO_x sampling problems are available to assist in the design of sampling systems.^{9–13} Additional information is available from a limited number of specialized combustion-related studies,^{14–17} from studies conducted to evaluate converter materials for chemiluminescent oxides of nitrogen analyzers,^{18–20} and from studies conducted to explore the catalytic oxidation of CO in automobile exhaust by O₂ and NO.^{21–23}

Table II. Homogeneous reactions.

Transformation	Reaction	Reference ^a		
		COMB	CONV	OTHER
<i>NO Oxidation</i>	(1) $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$	9, 14		58
<i>NO₂ Reduction</i>	(2) $2\text{NO}_2 \longrightarrow 2\text{NO} + \text{O}_2$		19	59
	(3) $\text{NO}_2 + \text{O} \longrightarrow \text{NO} + \text{O}_2$	17		
<i>NO_x Removal</i>	(4) ^b $\text{NO} + \text{CH} \longrightarrow \text{CHO} + \text{N}$	31, 32		

^a COMB: Combustion Related Study

CONV: Converter Related Study

^b CH: Hydrocarbon

Summaries of the transformation reactions that may be active in probes and sample lines are presented in Tables II, III, and IV for homogeneous, heterogeneous, and catalytic reactions, respectively. (Catalytic reactions may be either homogeneous or heterogeneous but are separately grouped here for convenience of presentation.) A review of the reactions is available.²⁴

The work of Halstead, Nation, and Turner¹⁴ is the most definitive study of chemical transformations of NO_x when sampling combustion products. Combustion products were sampled from a "Tunnel Mixing Burner" operating on natural gas and air. Two probe materials (stainless steel, 210 cm long × 6 mm I.D., and silica tubing, 210 cm long × 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 sample probe residence time was estimated to be 4 seconds. Lean fire conditions produced no change in NO_x concentrations for either the stainless steel or silica tubing. Changes were observed

for rich fire with the stainless steel probe. In particular, the NO_x concentration decreased in excess of 90%. No effect was observed for the silica. 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 extent to which the various reducing species (e.g. CO, H₂, and hydrocarbons) participate in the reduction and removal reactions cannot be assessed. In addition, the temperature gradient along the probe length prevents assessment of the sample conditions at which the reduction and removal reactions were activated.

A second study of note is reported by Few, Bryson, and McGregor.²⁵ Nitric oxide was measured at the exhaust plane of a gas turbine combustor using two methods—conventional probing and an optical technique. The NO concentrations measured optically ranged from 3 to 6 fold higher than those measured by conventional probing. Although important questions remain unanswered (e.g. the concentration of NO₂ and reducing species at the exhaust plane,

validation of the measurement of transmissivity, and the inlet pressure conditions and sensitivity of the chemiluminescent analyzer), the results reinforce the probability that NO_x may be removed within probes and sample lines under conditions encountered in practice.

Experimental

An adequate accounting of NO_x transformations requires that experiments be conducted to identify (1) the conditions for which chemical transformations occur, and (2) the extent to which they occur.

An experimental study has been initiated to assess NO_x transformations that may be encountered when sampling exhaust gas from practical combustion devices that operate air-rich (e.g. boilers, diesel engines, and gas turbine engines) and fuel-rich (e.g. automobile engines). A schematic of the experimental system is shown in Figure 1. The experimental system is designed 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, temperature, and probe material.

A carrier gas simulating the primary combustion products is selected from one of three prepared sources of 0, 1, and 5% O₂, 12% CO₂, and balance N₂. The carrier gas flow, 4 l/min, is doped with NO and NO₂ metered from high concentration source cylinders by means of porous sintered metal flow restrictors. Additional species are introduced in an identical manner. After doping, the carrier gas enters a silica preheat oven that raises the gas temperature to the desired probe test temperature. From

Table III. Heterogeneous reaction.

Transformation	Reaction	Reference ^a		
		COMB	CONV	OTHER
<i>NO Oxidation</i>	(5) $\text{NO} + \text{O} \xrightarrow{\text{wall}} \text{NO}_2$	17		
<i>NO₂ Reduction</i>	(6) $\text{NO}_2 + \text{metal} \xrightarrow{\text{wall}} \text{metal oxide} + \text{NO}$	34	20	
	(7) $\text{NO}_2 + \text{C} \xrightarrow{\text{wall}} \text{CO} + \text{NO}$	33	20, 60	
<i>NO_x Removal</i>	(8) $\text{NO}_2 \xrightarrow{\text{wall}} \text{absorbed adsorbed}$	9, 12, 14 34		35, 36
	(9) $\text{NO}_2 \xrightarrow{\text{condensate}} \text{absorbed}$	12, 37		
	(10) $\text{NO} + \text{C} \xrightarrow{\text{wall}} \text{CO} + \frac{1}{2} \text{N}_2$		20	
	(11) $\text{NO} + \text{metal} \xrightarrow{\text{wall}} \text{metal oxide} + \frac{1}{2} \text{N}_2$		29	
	(12) $\text{NO}_2 + \text{metal} \xrightarrow{\text{wall}} \text{metal oxide} + \frac{1}{4} \text{N}_2$		29	

^a COMB: Combustion Related Study

CONV: Converter Related Study

Table IV. Catalytic reactions.

Transformation	Reaction	Reference ^a		
		COMB	CONV	CAT
NO Oxidation	(13) $\text{NO} + \frac{1}{2} \text{O}_2 \longrightarrow \text{NO}_2$	9		
NO ₂ Reduction	(14) $\text{NO}_2 \longrightarrow \text{NO} + \frac{1}{2} \text{O}_2$	10	18, 19, 20, 34, 38	
NO _x Removal	(15) $\text{NO} + \text{CO} \longrightarrow \text{CO}_2 + \frac{1}{2} \text{N}_2$	9, 14		21, 22, 23
	(16) $5 \text{H}_2 + 2 \text{NO} \longrightarrow 2\text{NH}_3 + 2 \text{H}_2\text{O}$			30, 39, 40, 41

^a COMB: Combustion Related Study
 CONV: Converter Related Study
 CAT: Catalyst Study

this point, the doped carrier gas enters the test probe. A test probe oven is used to maintain the temperature of the doped carrier gas at the test temperature.

Test probe materials tested include 4.6 mm I.D. 316 stainless steel and silica glass (Vycor, Corning Glass Works). The length of each test probe is 2 m. The residence time of the doped carrier gas in the test probe is approximately 1/2 sec.

The gas temperature within the test probe is incrementally varied from 25° to 400°C. Temperatures of the gas stream (T₂ and T₃) are measured with insulated platinum resistance thermometers centered in the probe bore at the inlet and outlet of the test probe. The oven temperature is also recorded by a thermocouple located adjacent to the outer diameter of the test probe.

The NO and NO₂ input levels to the test probe (sample point 2) are chosen to be 500 ppm and 75 ppm respectively. These levels simulate a NO concentration selected as representative from Table I, and a NO₂ concentration which may be encountered in combustion source effluents.

The present paper reports on chemical transformations that occur in the presence and absence of O₂, CO, and H₂. Oxygen levels are taken to be 0, 1, and 5%; CO levels are taken to be 0, 100, 1000, and 2500 ppm; and hydrogen levels are taken to be 0, 0.5, and 3.0%.

Gas composition is measured at sample points 2 and 3 to assess the extent of NO and NO₂ transformation within the 2 m test probe. Gas composition is also measured at sample point 1 to assess whether chemical transformation occurs in the preheat oven. Sample lines leading from points 1, 2, and 3 are short, equidistant, and made of 6.4 mm (1/4 in.) O.D. TFE Teflon. Screening tests using varying lengths of the TFE Teflon were conducted to as-

sure that NO₂ adsorption was not a significant factor in the present experiment.

Analysis of NO and NO_x is conducted with a Beckman Model 951H chemiluminescent oxides of nitrogen analyzer. NO₂ is determined by the difference between the measured NO_x and NO concentrations. The (carbon) converter efficiency is tested following the procedure outlined in the Federal Register.³ Carbon monoxide and H₂ concentrations are measured using a Beckman Model 315BL nondispersive infrared analyzer, and a Beckman Model 7C thermal conductivity analyzer respectively.

Results

The results are presented in Figure 2 for oxidizing mixtures. Results for mixtures with CO are presented in Figure 3. Results for mixtures with H₂ are presented in Figure 4. The percent change of NO and NO₂ represents the percent change in concentration between sample

points 2 and 3 except where otherwise noted. In the figures, points above the horizontal temperature scale identify those cases for which total NO_x is conserved. In such cases, changes in NO concentration are proportional to changes in NO₂ concentration. Points below the horizontal temperature scale identify those cases for which NO_x is not conserved. The temperature shown is the gas temperature (maintained uniform) at sample points 2 and 3. The results reported are summarized from earlier presentations.^{24,26,27}

Oxygen

The results for silica are presented in Figure 2a. No significant transformation is observed over the temperature range and the residence time studied.

316 stainless steel (Figure 2b) catalytically reduces NO₂ to NO at gas temperatures in excess of 300°C. The conversion of NO₂ to NO at elevated temperatures is consistent with the results of a variety of chemiluminescent analyzer converter studies (Table IV). At temperatures below the catalytically active temperature, no significant change is observed.

Carbon Monoxide

The results for silica are presented in Figure 3a. No significant transformation is observed at temperatures up to and including 300°C. At 400°C, reduction of NO₂ to NO occurs.

The results for 316 stainless steel are presented in Figure 3b. NO₂ reduction is observed at 200°C and above. The reduction is more pronounced at the elevated levels of CO concentration.

The exposure history of the stainless steel test probe is observed to alter the degree of NO_x transformation. Temperature cycling and prolonged exposure to one condition stabilizes the repro-

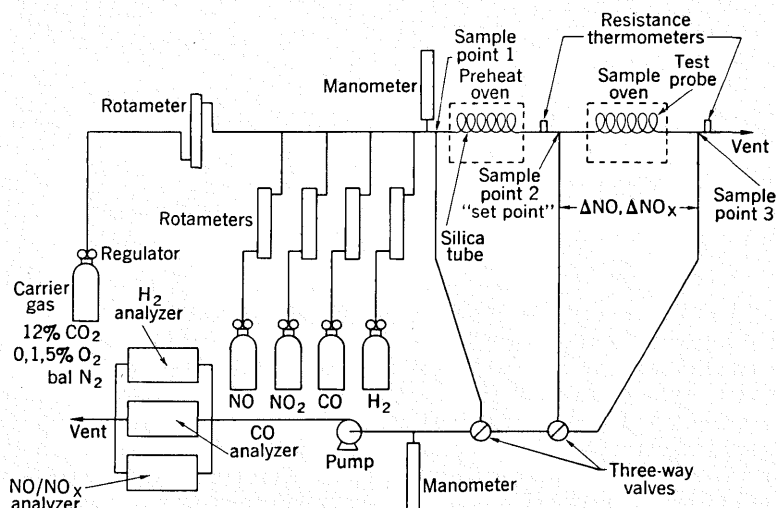


Figure 1. Experimental system.

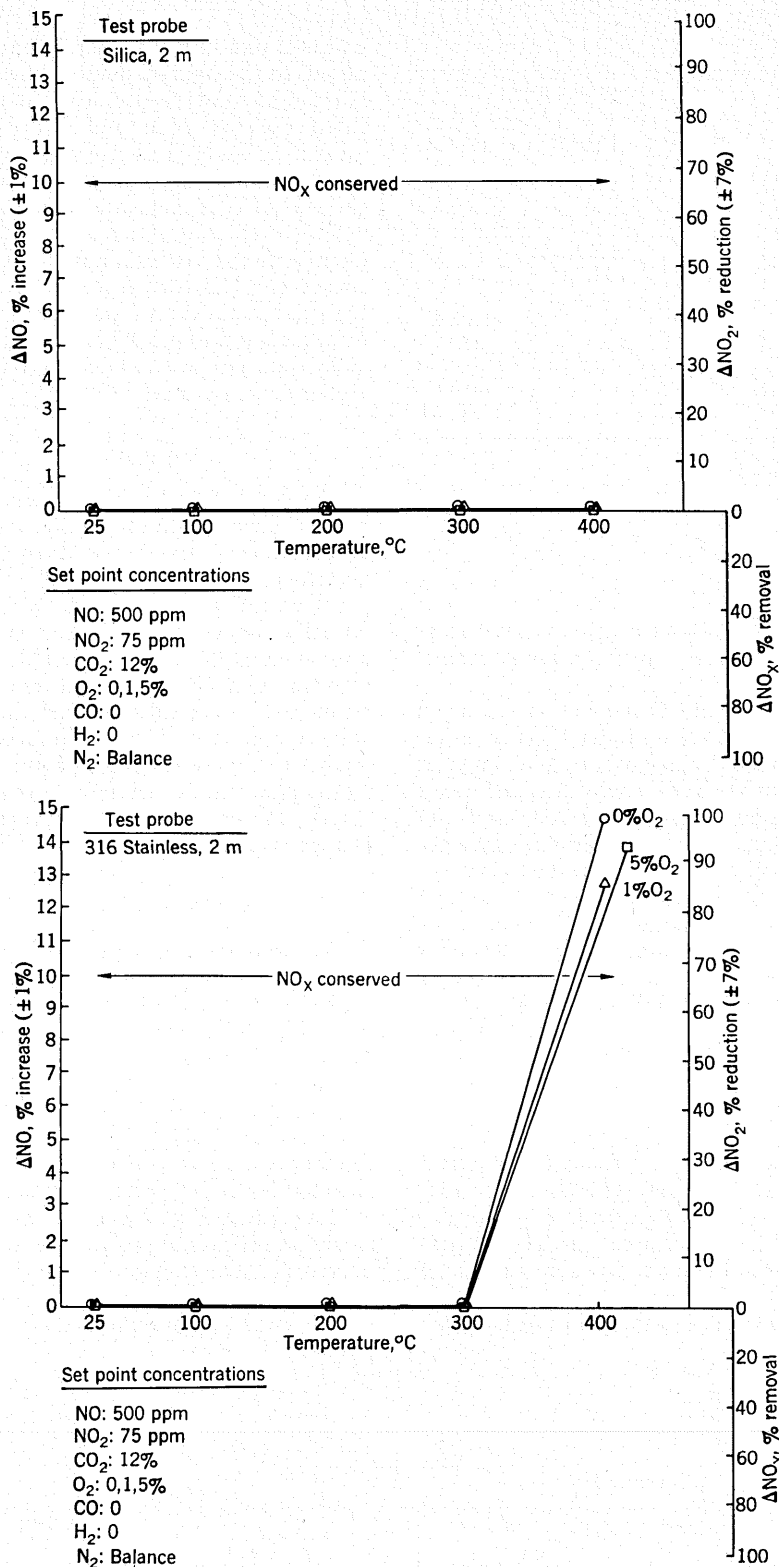


Figure 2. Results with oxidizing mixtures:²⁴ a) silica test probe; b) 316 stainless steel test probe.

ducibility of the results. The effect of probe history may, in part, be attributed to the condition of the inner wall. Reducing atmospheres degrade the protective oxide layer lining the inner wall of stainless tubes. Oxidizing atmospheres will renew the oxide layer. Other evidence of probe history effects have been reported in the literature,^{11,28} but

a full assessment has yet to be made. A controlled experiment is presently in progress to explore the effect of the stainless steel condition on nitrogen oxides transformation.

Of special note is the reduction of NO₂ observed in the silica preheat oven at the set point temperature of 400°C in the presence of CO. (For such cases, the NO₂

concentration must be increased and the NO concentration decreased at sample point 1 to maintain the set point condition—500 ppm NO, 75 ppm NO₂—at sample point 2.) The silica preheat tube is identical to the silica test probe including the length (2 m). An important distinction, however, must be kept in mind when interpreting the data. Namely, the temperature of the sample in the preheat oven is not uniform, but undergoes an excursion from the ambient to the set temperature.

Hydrogen

The results for H₂ are presented in Figure 4. Chemical transformations for two H₂ concentrations, 0.5% and 3%, are evaluated.

No significant chemical transformation in silica is observed up to and including 300°C (Figure 4a). At 400°C, the changes are dramatic and depend on H₂ concentration. At the lower H₂ concentration of 0.5%, the NO₂ is totally reduced in the silica preheat oven. At the elevated H₂ concentration of 3%, the NO_x is totally removed in the silica preheat oven. (Note that the set point concentration of 500 ppm NO, 75 ppm NO₂ at sample point 2 was not attained at 400°C. The concentrations of NO and NO₂ were increased at Sample Point 1 to offset the NO₂ reduction and NO_x removal in the silica preheat oven, but were limited in the present experiment to a maximum of 125 ppm NO₂, 890 ppm NO.)

The formation of CO was observed at 400°C with both test probes and 300°C with the stainless steel test probe. The CO concentrations increased with H₂ percent, and reached levels approaching 3500 ppm. The production of CO presumably results from the reduction of CO₂ by H₂. The presence of CO at the elevated temperatures likely contributes to the reduction of NO₂ and removal of NO_x observed.

Conclusions

- NO_x is conserved in silica and 316 stainless sample probes for the temperature range 25°–200°C and residence time of 1/2 sec in the presence of either CO, H₂, or O₂.
- NO_x is removed in 316 stainless steel probes at temperatures exceeding 200°C and in silica probes at temperatures exceeding 300°C in the presence of H₂.
- The removal of NO_x observed by Halstead, Nation, and Turner,¹⁴ and the difference between optical and probe measurements of NO observed by Few, Bryson, and McGregor²⁵ may be caused by the attack on NO by reducing species such as H₂ within the probe and sample line.

- Additional information is needed to guide the selection of probe and sample line materials in order to minimize the occurrence of transformations and to estimate the extent of transformations. In particular, the effect of residence time, sample pressure, surface to volume ratio, probe history, alternative materials, and the presence of hydrocarbon species and particulate matter need to be assessed.

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References

1. "Standards of performance for new stationary sources—proposed amendments to reference methods," *Federal Register* 41 (111):23059, (8 June, 1976).
2. "Control of air pollution from aircraft and aircraft engines," *Federal Register* 38 (136): 19088 (17 July, 1973).
3. "Control of air pollution from new vehicles and new motor vehicle engines," *Federal Register* 39 (101):18075 (23 May, 1974).
4. "Light-duty diesel powered trucks," *Federal Register* 39 (205):37610 (23 May, 1974).
5. "Emission regulation for new gasoline-fueled heavy duty engines," *Federal Register* 40 (40):8482 (27 Feb., 1975).
6. D. Latimer and G. S. Samuelsen, "Plume Visibility from Major Point Sources," Report No. UCI-ARTR-75-4, UCI Air Quality Laboratory, University of California, Irvine, Sept., 1975.
7. L. J. Muzio and R. P. Wilson, "Experimental Combustor for the Development of Package Boiler Emission Control Techniques," Report No. R2-73-292a, Environmental Protection Agency, July 1973.
8. K. R. Krumwiede, D. M. Norton, G. W. Johnson, R. E. Thompson, B. P. Breen, and V. Quan, "A Probing Study of NO Formation in the Flame Zone of a 175 MW Gas Fired Utility Boiler," Paper No. 75-23.4, 68th Annual Meeting of the Air Pollution Control Association, June, 1975.
9. C. J. Halstead and A. J. E. Munro, "The Sampling, Analysis and Study of the Nitrogen Oxides found in Natural Gas/Air Flames," I.G.T/A.G.A. Conference on National Gas Research and Technology, Chicago, IL, 1971.
10. C. J. Halstead, "Sampling and Analysis of Combustion Products for Nitrogen

11. J. H. Tuttle, R. A. Shisler, and A. M. Mellor, "Nitrogen Dioxide Formation in Gas Turbine Engines: Measurements and Measurement Methods," Report PURDU-CL-73-06, Grant R-801284, Environmental Protection Agency, Dec., 1973.

12. J. D. Allen, "A review of methods of analysis for oxides of nitrogen," *J. Inst. Fuel* 46 (384):123 (1973).
13. J. D. Allen, J. Billingsley, and J. T. Shaw, "Evaluation of the measurement of oxides of nitrogen in combustion products by the chemiluminescence method," *J. Inst. Fuel* 47 (393):275 (1974).
14. C. J. Halstead, G. H. Nation, and L.

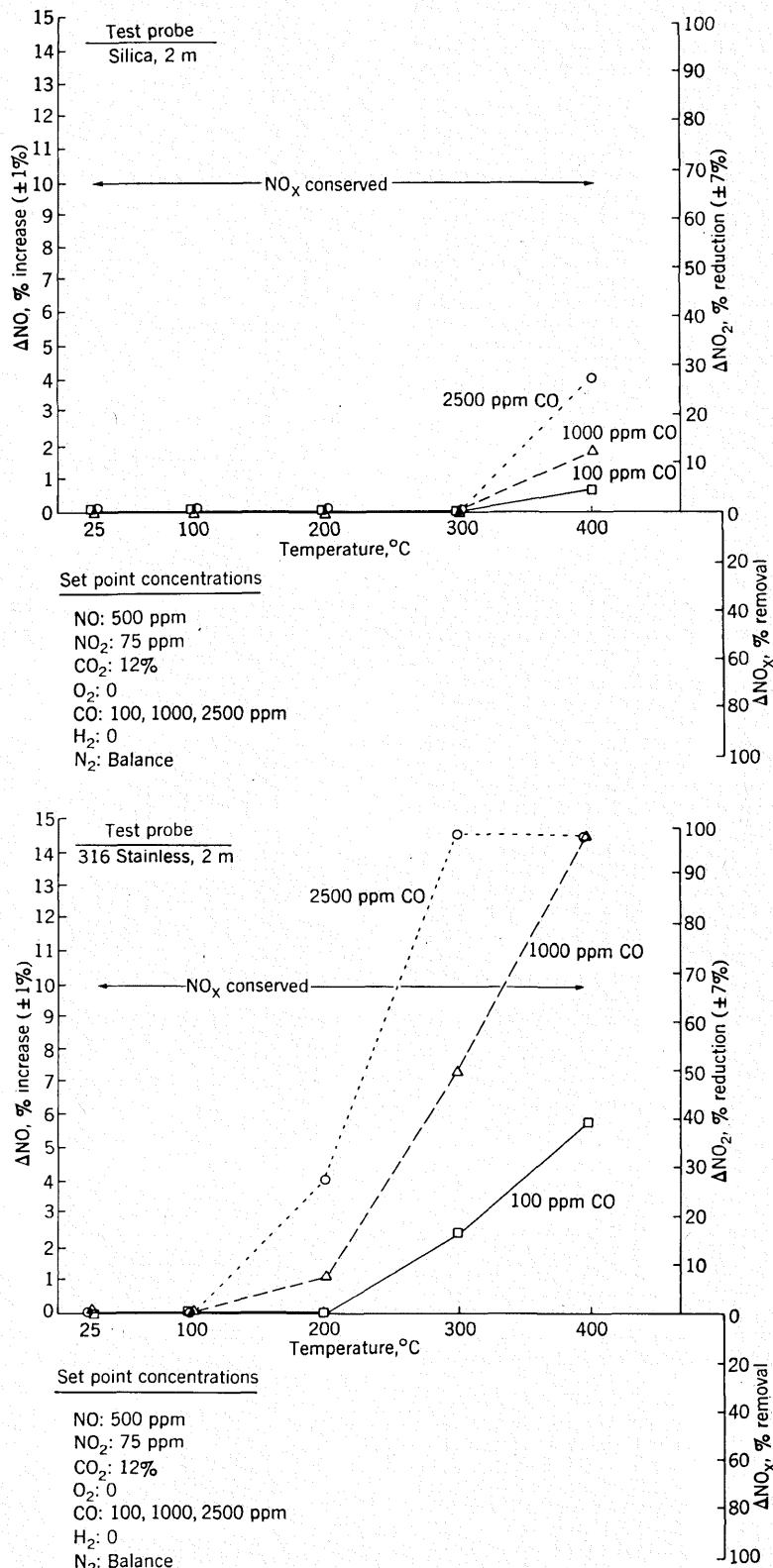


Figure 3. Results with carbon monoxide:²⁶ a) silica test probe; b) 316 stainless steel test probe.

Turner, "The determination of nitric oxide and nitrogen dioxide in flue gas," *Analyst* 97:55 (1972).

15. E. England, J. Houseman, and D. P. Teixeira, "Sampling nitric oxide from combustion gases," *Combust. Flame* 20:439 (1973).
16. R. W. Schefer, R. D. Matthews, N. P. Cernansky, and R. F. Sawyer, "Measurement of NO and NO₂ in Combustion Systems," Paper No. WSS/CI 73-31, 1973 Fall Meeting of the Western States Section/The Combustion Institute, El Segundo, CA, Oct., 1973.
17. J. D. Allen, "Probe sampling of oxides of nitrogen from flames," *Combust. Flame* 24:133 (1975).
18. J. A. Hodgeson, J. P. Bell, K. A. Rehme, K. J. Krost, and R. K. Stevens, "Application of a Chemiluminescence Detector for the Measurement of Total Oxides of Nitrogen and Ammonia in the Atmosphere," Paper No. 71-1067, presented at 64th Annual Meeting of APCA, 1971.
19. J. E. Sigsby, F. M. Black, T. A. Bellar, and D. L. Klosterman, "Chemiluminescent method for analysis of nitrogen compounds in mobile source emissions (NO, NO₂, and NH₃)," *Environ. Sci. Technol.* 7 (1):51 (1973).
20. L. P. Breitenbach and M. Shelef, "Development of a method for the analysis of NO₂ and NH₃ by NO-measuring instruments," *J. Air Poll. Control Assoc.* 23 (2):128 (1973).
21. R. A. Baker and R. C. Doerr, "Catalyzed nitric oxide reduction with carbon monoxide," *Ind. Eng. Chem., Process Design Develop.* 4 (2):189 (1965).
22. M. Shelef, K. Otto, and H. Gandhi, "The oxidation of CO by O₂ and by NO on supported chromium oxide and other metal oxide catalysts," *Catalysis* 12:361 (1968).
23. J. R. Aven and Y. Ng, "Catalytic reduction of nitric oxide by carbon monoxide," *Int. J. Air Water Poll.* 10 (1):1 (1966).
24. G. S. Samuelsen and J. Harman, "Transformation in Oxides of Nitrogen Concentration While Sampling Combustion Products," Presented at the 1st International Chemical Congress, Western Hemisphere, American Chemical Society, Mexico City 1975.
25. J. D. Few, R. J. Bryson, and W. K. McGregor, "Evaluation of Probe Sampling Versus Optical In Situ Measurements of Nitric Oxide Concentrations in a Jet Engine Combustor Exhaust," Report AEDC-TR-76-180, Arnold Engineering Development Center, Jan., 1977.
26. R. Benson, G. S. Samuelsen, and R. E. Peck, "Oxides of Nitrogen Transformation While Sampling Combustion Products Containing Carbon Monoxide," WSS/CI Paper 76-11, 1976 Spring Meeting of the Western States Section/The Combustion Institute, Salt Lake City, UT, 1976.
27. R. Benson and G. S. Samuelsen, "Oxides of Nitrogen Transformation While Sampling Combustion Products Containing Carbon Monoxide and Hydrogen," WSS/CI Paper 76-39, 1976 Fall Meeting of the Western States Section/The Combustion Institute, La Jolla, CA, 1976.
28. E. E. Peterson, J. Landau, and E. Squedo, "Micro and Macro Changes in a Stainless Steel Catalyst During Reduction of NO," in R. L. Klimisch and J. G. Larson (eds.), *The Catalytic Chemistry of Nitrogen Oxides*, Plenum Press, New York, 1975, pp 119-131.
29. Robert M. Siewert, "Hydrogen interference in chemiluminescent NO_x analysis," *Combust. Flame* 25:273 (1975).
30. A. Lamb and E. L. Tollefson, "Catalytic

reduction of nitric oxide in the presence of oxygen in low concentration high velocity gas streams," *Can. J. Chem. Eng.* 53(1):68 (1975).

31. A. L. Myerson, "The Reduction of Nitric Oxide in Simulated Combustion Effluents by Hydrocarbon-Oxygen Mix-

ture," *Fifteenth Symposium (International) on Combustion*, The Combustion Institute, 1975 pp 1085-1092.

32. A. L. Myerson and D. W. Blair, "Reduction of nitric oxide in automobile engine exhaust by ethane-air injection," *Environ. Sci. Technol.* 10 (5):461 (1976).

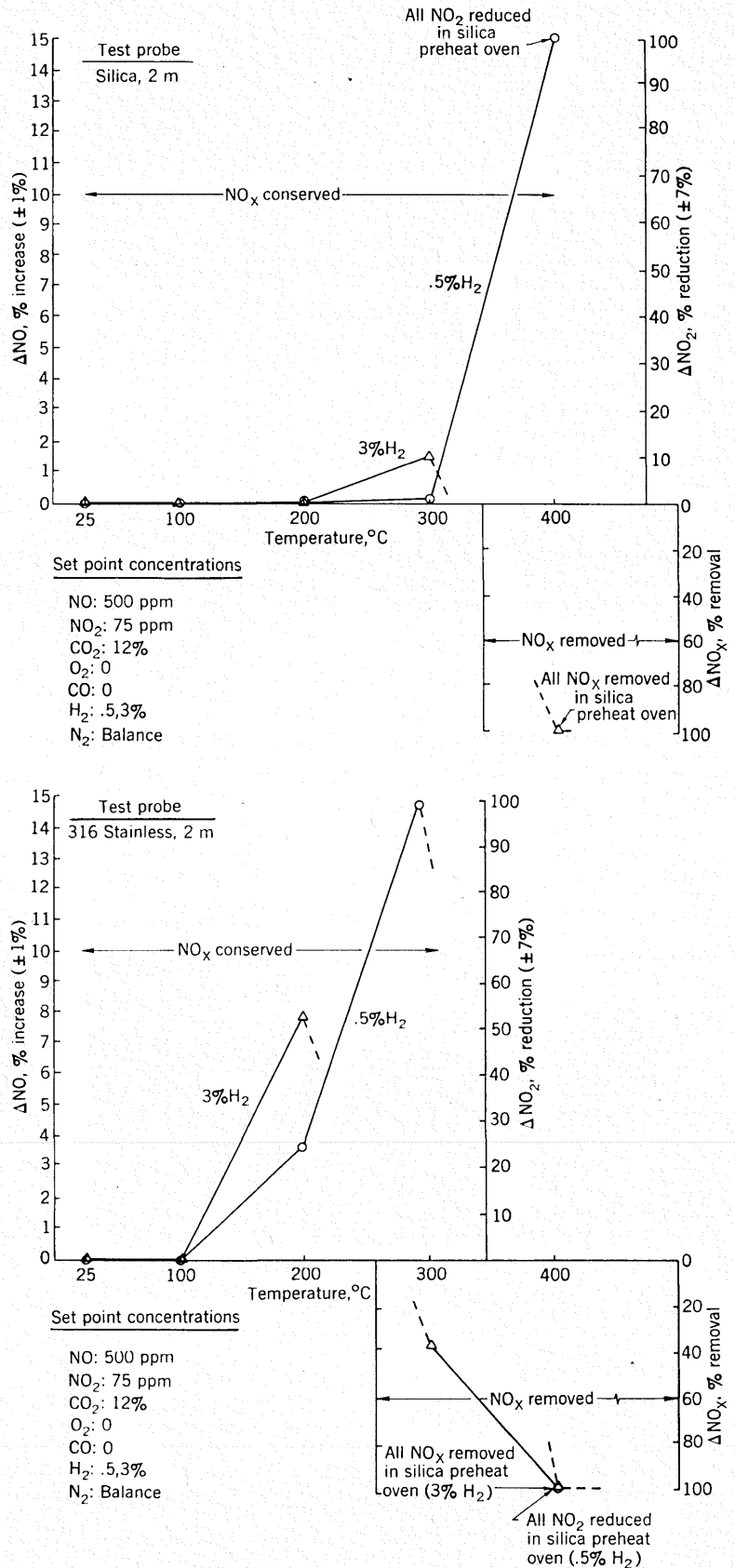


Figure 4. Results with hydrogen:²⁷ a) silica test probe; b) 316 stainless steel test probe.

33. N. P. Cernansky, "Formation of NO and NO₂ in a Turbulent Propane/Air Diffusion Flame," Report No. ME-74-5, Ph.D. Dissertation, Department of Mechanical Engineering, University of California, Berkeley, 1974.
34. A. White, and L. M. Beddows, "The choice of sampling tube material in the determination of nitrogen oxide concentrations in products of combustion," *J. Appl. Chem. Biotechnol.* 23:759 (1973).
35. T. E. Healy and P. Urone, "Gas chromatography of oxidants using a flowing liquid colorimetric detector," *Anal. Chem.* 41:1777 (1969).
36. A. Lebovits, "Permeability of polymers of gases, vapors, and liquid," *Modern Plastics*, 139 (1966).
37. K. J. McNulty, J. F. McCoy, J. H. Becker, J. R. Ehrenfeld, and R. L. Goldsmith, "Investigation of Extractive Sampling Interface Parameters," Report EPA-650/2-74-089, Environmental Protection Agency, Dec., 1974.
38. E. Sherwin and C. J. Weston, *Chemistry of the Non-Metallic Elements*, Pergamon Press, New York 1966.
39. M. Shelef and H. S. Gandhi, "Ammonia formation in the catalytic reduction of nitric oxide. III. The role of water gas shift, reduction by hydrocarbons, and steam reforming," *Ind. Eng. Chem. Prod. Res. Develop.* 13 (1):80 (1974).
40. R. L. Klimisch and G. J. Barnes, "Chemistry of catalytic nitrogen oxide reduction in automobile exhaust gas," *Environ. Sci. Technol.* 6 (6):543 (1972).
41. R. L. Klimisch and K. C. Taylor, "Ammonia intermediary as a basis for catalyst selection for nitric oxide reduction," *Environ. Sci. Technol.* 7 (2):127 (1973).
42. V. A. Zuonow, H. E. Stewart, and E. S. Starkman, "Hydraulically actuated combustion gas sampling valve," *Rev. Sci. Instr.* 39 (12):1820 (1967).
43. M. Alperstein and R. Bradow, "Combustion gas sampling valve," *Rev. Sci. Instr.* 36 (7):1028 (1965).
44. J. E. Bennethum, N. J. Mattavi, and R. R. Toepel, "Diesel Combustion Chamber Sampling—Hardware, Procedures and Data Interpretation," SAE Paper 750849, Society of Automotive Engineers, 1975.
45. R. E. Barrett, S. E. Miller, and D. W. Locklin, "Field Investigation of Emissions from Combustion Equipment for Space Heating," Final Report, Contract 68-02-0251, Environmental Protection Agency, June, 1973.
46. W. Bartok, A. Crawford, and G. Piegari, "Systematic Field Study of NO_x Emission Control Methods for Utility Boilers," Report No. APTD-1163, Environmental Protection Agency, Dec. 1971.
47. G. A. Cato and J. M. Robinson, "Application of Combustion Modification Techniques to Control Pollutant Emissions from Industrial Boilers—Phase I," Final Report, Contract 68-02-1074, Environmental Protection Agency, Sept., 1974.
48. D. C. Davidson and A. F. Domal, "Emission Measurements of a J93 Turbojet Engine," Report No. AEDC TR 73-132, Arnold Engineering Development Center, Sept., 1973.
49. W. S. Blazowski and R. E. Henderson, "Assessment of Pollutant Measurement and Control Technology and Development of Pollutant Reduction Goals for Military Aircraft Engines," Report No. AFAPL-TR-72-102, Air Force Aero Propulsion Laboratory, Nov., 1972.
50. J. H. Elwood and R. H. Dieck, "Techniques and Procedures for the Measurement of Aircraft Gas Turbine Engine Emission," APCA Paper 74-90, 67th Annual Meeting, Air Pollution Control Association, Denver, CO, June 1974.
51. J. W. Grossman, J. H. Slaminski, and A. Licata, "Emission Data and Combustion Calculations for a General Electric PG-5341 Gas Turbine," WSS/CI Paper 74-5, 1974 Spring Meeting of the Western States Section/The Combustion Institute, Pullman, Washington, Apr. 1974.
52. N. P. Cernansky and R. F. Sawyer, "NO and NO₂ Formation in a Turbulent Hydrocarbon/Air Diffusion Flame," *Fifteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 1975 pp 1039-1050.
53. E. L. Merryman and A. Levy, "Nitrogen Oxide Formation in Flames," *Fifteenth Symposium (International) on Combustion*, The Combustion Institute, 1975 pp 1073-1083.
54. C. P. Fenimore, "Formation of Nitric Oxide in Premixed Hydrocarbon Flames," *Thirteenth Symposium (International) on Combustion*, The Combustion Institute, 1971 pp 373-380.
55. C. P. Fenimore, "The ratio NO₂/NO in fuel-lean flames," *Combust. Flame* 25:85 (1975).
56. F. Pompei and J. B. Heywood "The role of mixing in burner-generated carbon monoxide and nitric oxide," *Combust. Flame* 19:407 (1972).
57. P. C. Malte and D. T. Pratt, "Oxides of Nitrogen Formation for Fuel-Lean Jet-Stirred Carbon Monoxide Combustion," WSS/CI Paper No. 73-37, 1973 Fall Meeting of the Western States Section/The Combustion Institute, El Segundo, CA, Oct., 1973.
58. D. H. Stedman, E. E. Daby, F. Stuhl, and H. Niki, "Analysis of ozone and nitric oxide by chemiluminescent method in laboratory and atmospheric studies of photochemical smog," *J. Air Poll. Control Assoc.* 22 (4):260 (1972).
59. W. A. Rosser and H. Wise, "Thermal decomposition of nitrogen dioxide," *J. Chem. Phys.* 24:493 (1956).
60. R. K. Stevens, T. Clark, R. Baumgardner, and J. Hodgeson, "Instrumentation for the Measurement of Nitrogen Dioxide," in *Instrumentation for Monitoring Air Quality*, ASTM Pub. 04-555000-17, American Society for Testing and Materials, 1973.