Title
Chemical transformations of nitrogen oxides while sampling combustion products

Permalink
https://escholarship.org/uc/item/18h7v2j3

Journal
Journal of the Air Pollution Control Association, 27(7)

ISSN
0002-2470

Authors
Samuelsen, GS
Harman, JN

Publication Date
1977

DOI
10.1080/00022470.1977.10470467

License
CC BY 4.0

Peer reviewed
Chemical Transformations of Nitrogen Oxides While Sampling Combustion Products

G. S. Samuelsen and John N. Harman, III
University of California, Irvine, California

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\textsubscript{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\textsubscript{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\textsubscript{2} to NO is observed in 316 stainless steel at temperatures in excess of 100°C, and reduction of NO\textsubscript{2} to NO in silica is observed at 400°C. In the presence of H\textsubscript{2}, NO\textsubscript{2} is reduced to NO in 316 stainless steel at 200°C and NO\textsubscript{2} is removed at temperatures exceeding 200°C. In silica, the presence of H\textsubscript{2} promotes the reduction of NO\textsubscript{2} to NO at 300°C and the removal of NO\textsubscript{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 instrumentation 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\textsubscript{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:** NO $\rightarrow$ NO\textsubscript{2}  
  NO\textsubscript{x} conserved

- **NO\textsubscript{2} Reduction:** NO\textsubscript{2} $\rightarrow$ NO  
  NO\textsubscript{x} conserved

- **NO\textsubscript{2} Removal:** NO, NO\textsubscript{2} $\rightarrow$ N\textsubscript{2}  
  NO\textsubscript{x} not conserved

An additional transformation path, formation, involves the oxidation of nitrogen containing species such as ammonia (NH\textsubscript{3}). Because formation of NO\textsubscript{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\textsubscript{x} control, or from flames into which nitrogen containing compounds have been injected to study fuel bound NO\textsubscript{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
Table I. Sampling conditions for nitrogen oxides.

<table>
<thead>
<tr>
<th>Source</th>
<th>Typical NO(_x) ppm</th>
<th>Sampling point</th>
<th>Typical sampling environment</th>
<th>Examples of NO(_x) Probing</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal combustion engine</td>
<td>500-4000</td>
<td>Combustion zone</td>
<td>1300–2400 Reducing</td>
<td>42,43</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>500–1000</td>
<td>Engine exhaust</td>
<td>200–500 Reducing</td>
<td>3,5</td>
<td></td>
</tr>
<tr>
<td>Diesel engine</td>
<td>1000–7000</td>
<td>Combustion zone</td>
<td>700–2500 Reducing and Oxidizing</td>
<td>4</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>700–2500</td>
<td>Engine exhaust</td>
<td>200–500 Oxidizing</td>
<td>45</td>
<td>14</td>
</tr>
<tr>
<td>Residential oil burners</td>
<td>20–100</td>
<td>Flue gas</td>
<td>100–300 Oxidizing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boilers</td>
<td>200–1000</td>
<td>Combustion zone</td>
<td>100–1600 Reducing and Oxidizing</td>
<td>7,8</td>
<td>15,16,17</td>
</tr>
<tr>
<td></td>
<td>25–800</td>
<td>Flue gas</td>
<td>100–300 Oxidizing</td>
<td>1,46,47</td>
<td>14</td>
</tr>
<tr>
<td>Gas turbine</td>
<td>1000–8000</td>
<td>Combustion zone</td>
<td>1500–2700 Reducing and Oxidizing</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25–200</td>
<td>Engine exhaust</td>
<td>400–1500 Oxidizing</td>
<td>25,48,49,50,51</td>
<td>11,14</td>
</tr>
<tr>
<td>Flame research</td>
<td>10–8000</td>
<td>Within flame</td>
<td>700–2500 Reducing and Oxidizing</td>
<td>52,53,54,55,56,57</td>
<td>15,16,17</td>
</tr>
</tbody>
</table>

promulgated in terms of nitrogen oxides, NO\(_x\).\(^{1,2,3}\) As a result, the enforcement of emission standards is not compromised by the occurrence of NO oxidation or NO\(_x\) 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 NO\(_x\) reduction reactions in probes and sample lines warrants increased attention as well. For example:

1. **Assessment of local air quality impact**
   The NO/NO\(_x\) emission ratio is important in assessing local air quality impact from major sources. Ambiguity regarding the NO/NO\(_x\) emission ratio from combustion sources presently precludes consideration of the impacts of NO and NO\(_x\) on areas in proximity to the source.

2. **Assessment of plume visibility impact**
   The NO/NO\(_x\) emission ratio is important in the prediction of plume visibility from power plants.\(^{4}\
   The ambiguity regarding the NO/NO\(_x\) 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 NO\(_x\). Ambiguity regarding the NO/NO\(_x\) 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 NO\(_x\) within flames are required to assess the chemical kinetic mechanisms responsible for the formation of NO\(_x\). Questions attendant to transformation of NO and NO\(_x\) in sample probes presently limit the utility of fundamental studies that address NO and NO\(_x\) 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:

<table>
<thead>
<tr>
<th>Temperature Group</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moderate</td>
<td>25°–600°C</td>
</tr>
<tr>
<td>High</td>
<td>600°–1200°C</td>
</tr>
<tr>
<td>Very high</td>
<td>1200°–2500°C</td>
</tr>
</tbody>
</table>

**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 O\(_2\) and NO.\(^{21–23}\)
Table II. Homogeneous reactions.

<table>
<thead>
<tr>
<th>Transformation</th>
<th>Reaction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO Oxidation</td>
<td>NO + O → 2 NO₂</td>
<td>COMB 9, 14 CONV 19 OTHER 59</td>
</tr>
<tr>
<td>NO₂ Reduction</td>
<td>NO₂ + metal → metal oxide + NO</td>
<td>COMB 34 CONV 20</td>
</tr>
<tr>
<td>NO₂ Removal</td>
<td>NO₂ adsorbed → NO₂ condensate</td>
<td>COMB 9, 12, 14 CONV 34 OTHER 35, 36</td>
</tr>
</tbody>
</table>

Table III. Heterogeneous reaction.

<table>
<thead>
<tr>
<th>Transformation</th>
<th>Reaction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO Oxidation</td>
<td>NO + O → NO₂</td>
<td>COMB 17</td>
</tr>
<tr>
<td>NO₂ Reduction</td>
<td>NO₂ + metal → metal oxide + NO</td>
<td>CONV 34 OTHER 20</td>
</tr>
<tr>
<td>NO₂ Removal</td>
<td>NO₂ + metal → metal oxide + N₂</td>
<td>COMB 20 OTHER 29, 29</td>
</tr>
</tbody>
</table>

References:

1. COMB: Combustion Related Study
2. CONV: Converter Related Study
3. OTHER
4. CH: Hydrocarbon
5. A second study of note is reported by Few, Bryson, and McGregor.
6. A review of the reactions is available.
7. The work of Halstead, Nation, and Turner is the most definitive study of homogeneous, heterogeneous, and catalytic reactions, respectively.
8. 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.
10. 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 NOx may be removed within probes and sample lines under conditions encountered in practice.

Experimental

An adequate accounting of NOx 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 NOx 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 O₂, CO, and 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.
Table IV. Catalytic reactions.

<table>
<thead>
<tr>
<th>Transformation</th>
<th>Reaction</th>
<th>COMB</th>
<th>CONV</th>
<th>CAT</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NO Oxidation</strong></td>
<td>(13) NO + ( \frac{1}{2} ) O(_2) ( \rightarrow ) NO(_2)</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>NO(_2) Reduction</strong></td>
<td>(14) NO(_2) ( \rightarrow ) NO + ( \frac{1}{2} ) O(_2)</td>
<td>10</td>
<td>18, 19, 20, 34, 38</td>
<td></td>
</tr>
<tr>
<td><strong>NO(_x) Removal</strong></td>
<td>(15) NO + CO ( \rightarrow ) CO(_2) + ( \frac{1}{2} ) N(_2)</td>
<td>9, 14</td>
<td>21, 22, 23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(16) 5 H(_2) + 2 NO ( \rightarrow ) 2NH(_3) + 2 H(_2)O</td>
<td>30, 39, 40, 41</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) 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 \( \frac{1}{2} \) sec.

The gas temperature within the test probe is incrementally varied from 250°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 test probe. The oven temperature is also recorded by a thermocouple located adjacent to the outer diameter of the test probe.

The NO and NO\(_2\) 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 of 500 ppm and 75 ppm 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 H\(_2\) are presented in Figure 4. The percent change in NO and NO\(_2\) 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\(_2\) is conserved. In such cases, changes in NO concentration are proportional to changes in NO\(_2\) concentration. Points below the horizontal temperature scale identify those cases for which NO\(_2\) 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.\(^{34,36,37}\)

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 NO\(_2\) to NO at gas temperatures in excess of 300°C. The conversion of NO\(_2\) to NO 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 NO\(_2\) to NO occurs.

The results for 316 stainless steel are presented in Figure 3b. NO\(_2\) reduction is observed at 300°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\(_2\) transformation. Temperature cycling and prolonged exposure to one condition stabilizes the repro-

![Experimental system](image-url)
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, 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 NOx 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 NOx 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 NOx and removal of NOx observed.

Conclusions

- NOx is conserved in silica and 316 stainless sample probes for the temperature range 25°C-200°C and residence time of 1/4 sec in the presence of either CO, H2, or O2.
- NOx 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 NOx 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.

Acknowledgments

This study was performed at the UCI Combustion Laboratory and sponsored in part by a grant from the Air Force Office of Scientific Research, under Grant No. AFOSR-74-2710, and by the Institute of Transportation Studies (ITS) Transit Management Program and the State of California. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation hereon.

The authors wish to extend their appreciation to Daniel E. Bleeker and Ronald Benson (collection of data), and Dewey Baker and John Taylor (design of the experimental system and maintenance of the instrumentation).

References

14. C. J. Halstead, G. H. Nation, and L.


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


