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MEASUREMENT OF NO AND NO<sub>2</sub> IN COMBUSTION  
SYSTEMS

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The measurement of NO and NO <sub>2</sub> was studied in a premixed opposed jet stabilized flame and in a simple trubulent diffusion flame using propane and air in both cases. Cooled and uncooled quartz and stainless steel gas sampling probes, with tips designed to provide aerodynamic quenching, were used and compared. Concentration measurements were made with a chemiluminescent nitric oxide detector modified for the additional measurement of total NO <sub>x</sub> . All probes yielded similar results for total NO <sub>x</sub> concentrations. There were, however,		

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substantial differences in the NO and NO<sub>2</sub> measurements, since the uncooled probes promoted the reduction of NO<sub>2</sub> to NO. Substantial quantities of NO<sub>2</sub> were observed in both combustion systems.

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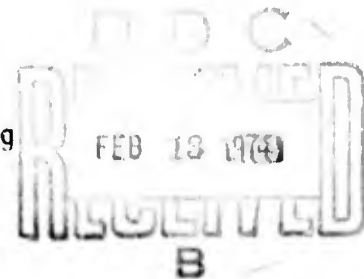
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MEASUREMENT OF NO AND NO<sub>2</sub> IN COMBUSTION SYSTEMS\*

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Abstract

The measurement of NO and NO<sub>2</sub> was studied in a premixed opposed jet stabilized flame and in a simple turbulent diffusion flame using propane and air in both cases. Cooled and uncooled quartz and stainless steel gas sampling probes, with tips designed to provide aerodynamic quenching, were used and compared. Concentration measurements were made with a chemiluminescent nitric oxide detector modified for the additional measurement of total NO<sub>x</sub>.

All probes yielded similar results for total NO<sub>x</sub> concentrations. There were, however, substantial differences in the NO and NO<sub>2</sub> measurements, since the uncooled probes promoted the reduction of NO<sub>2</sub> to NO. Substantial quantities of NO<sub>2</sub> were observed in both combustion systems.

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## INTRODUCTION

In late 1971, Airesearch Manufacturing Company reported measuring nitrogen dioxide in significant concentrations in the exhaust of gas turbines of their manufacture,<sup>(1)</sup> Figure 1. As a preliminary check of the Airesearch results, centerline  $\text{NO}_x$  profiles, Figure 2, were measured in our laboratory model gas turbine combustor. Until these measurements were taken it had been generally accepted that  $\text{NO}_2$  constituted, at most, 5% of the total oxides of nitrogen in emissions from this category of combustion system.<sup>(2,3,4)</sup> Since both of these experiments demonstrated levels well above both previously reported results and equilibrium predictions, it was felt that an investigation of  $\text{NO}_x$  measuring techniques was warranted.

Measurements of  $\text{NO}$ ,  $\text{NO}_2$  and total  $\text{NO}_x$  were made in two distinct combustion systems using four different types of gas sampling probes. The objective of the research was to closely examine the gas sampling system to determine whether or not it was a source of significant error in the analysis of the oxides of nitrogen.

## EXPERIMENT

### Combustion Systems

A simple turbulent diffusion flame and a premixed opposed jet stabilized flame were used for the study. These two systems were selected because of their stability, reproducibility and representation of two distinct combustion configurations.

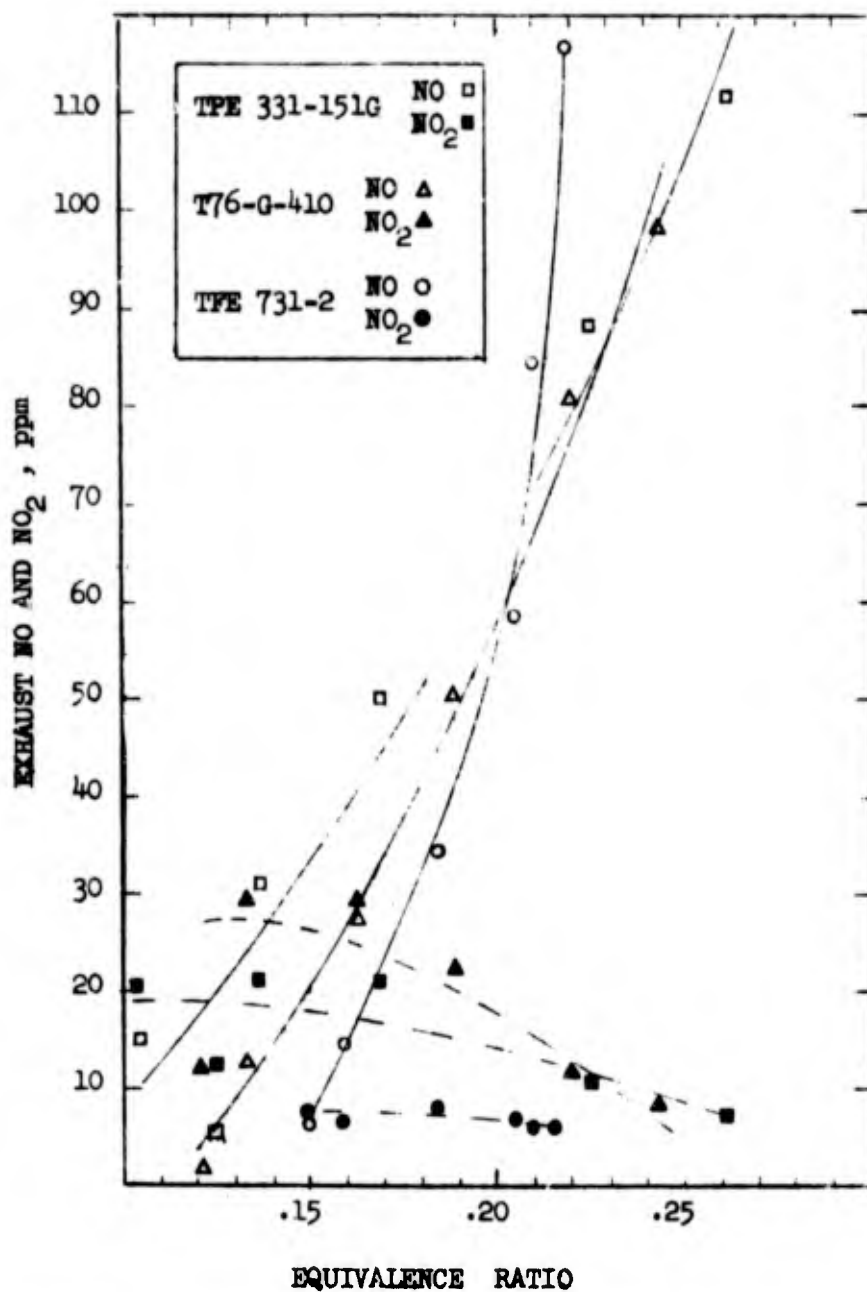


FIGURE 1. Results of Airesarch's investigation for three typical gas turbines.<sup>1</sup>

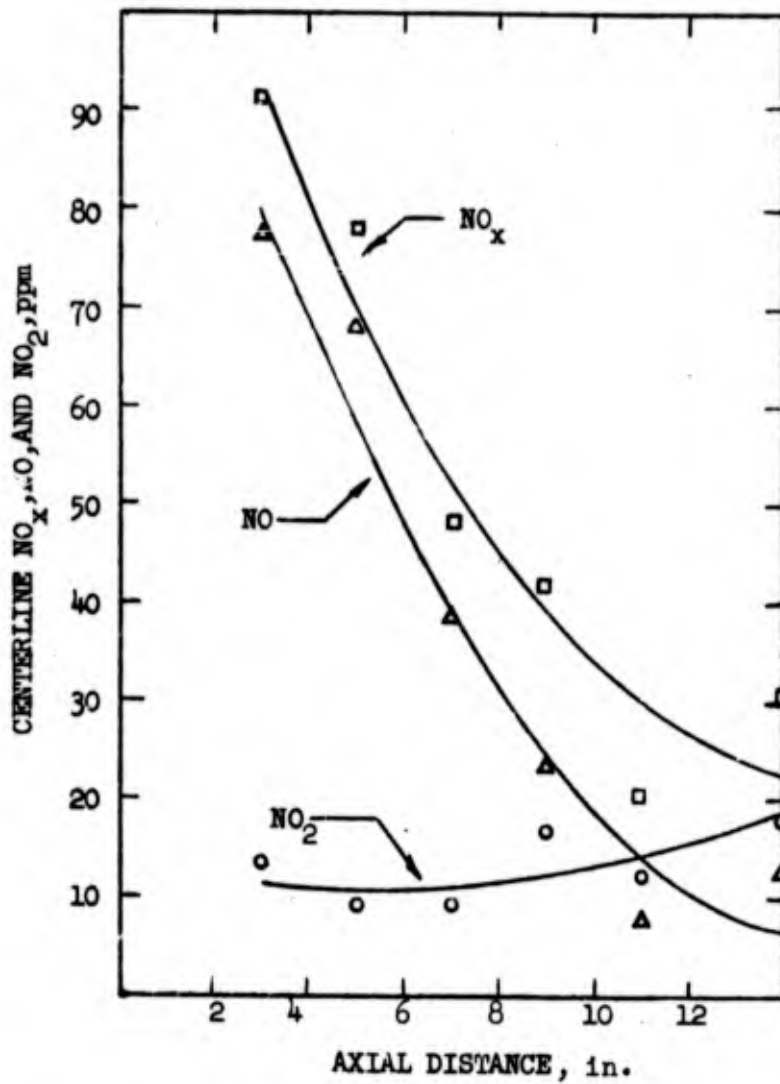


FIGURE 2. Oxides of nitrogen distribution in model gas turbine combustor.

The same combustion tunnel was used for both configurations. The combustion tunnel consisted of a horizontal 58 mm I.D. x 356 mm Vycor liner which contained the flame. For the turbulent diffusion flame, Figure 3, propane was injected coaxially through an 8.7 mm I.D. x 0.4 mm wall type 304 stainless steel tube located 152 mm into the combustor and mixed with a swirled air flow which was introduced via the Vycor pipe. In the case of the premixed opposed jet stabilized flame, Figure 4, a propane-air mixture of equivalence ratio 0.81 was injected through a water cooled jet located 64 mm from the combustor exit. This jet of fuel and air was introduced 180° from the flow direction of the incoming main stream mixture of the same equivalence ratio. In all cases the reactants were initially at ambient temperature and the combustion carried out at one atmosphere pressure.

#### Sampling probes:

Because of concern over possible catalytic probe effects,<sup>(5)</sup> cooled and uncooled quartz and cooled and uncooled stainless steel sampling probes were used and compared. All probes were designed to provide aerodynamic quenching by expanding the sample gases to low pressure across an orifice, yielding a quench time on the order of the expansion time. For choked flow through a short 0.1 to 0.25 mm diameter orifice, this time is in microseconds giving an initial quench rate of the order 100°K/μsec.

The cooled probes were of standard triple wall construction and are shown schematically in Figures 5 and 6. The uncooled quartz probe, Figure 7, was simply quartz tubing drawn to a taper and firepolished to an orifice. The uncooled stainless steel probe, Figure 8, which was

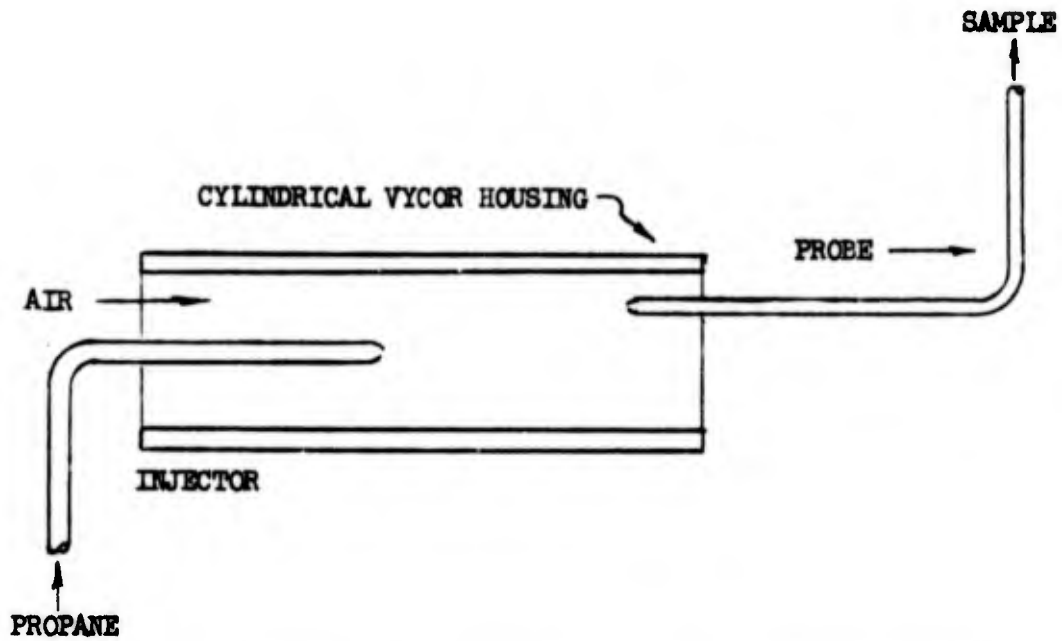


FIGURE 3. Configuration of turbulent diffusion combustion system.

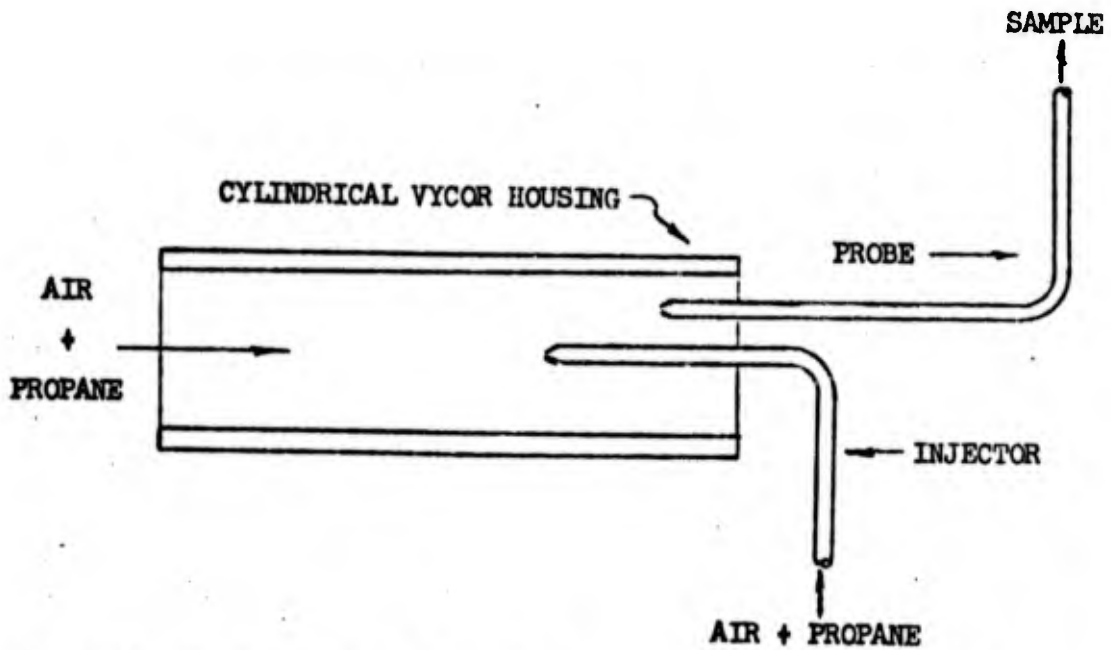


FIGURE 4. Configuration of premixed opposed jet combustion system.

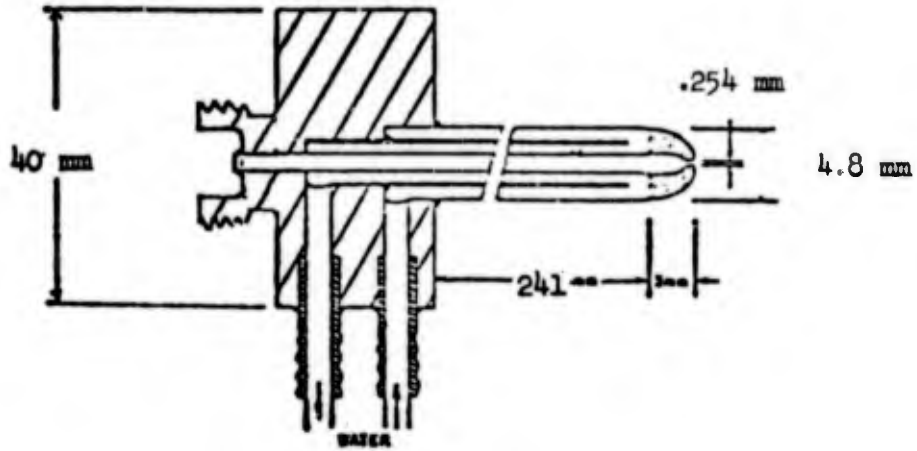


FIGURE 5. Watercooled stainless steel probe.

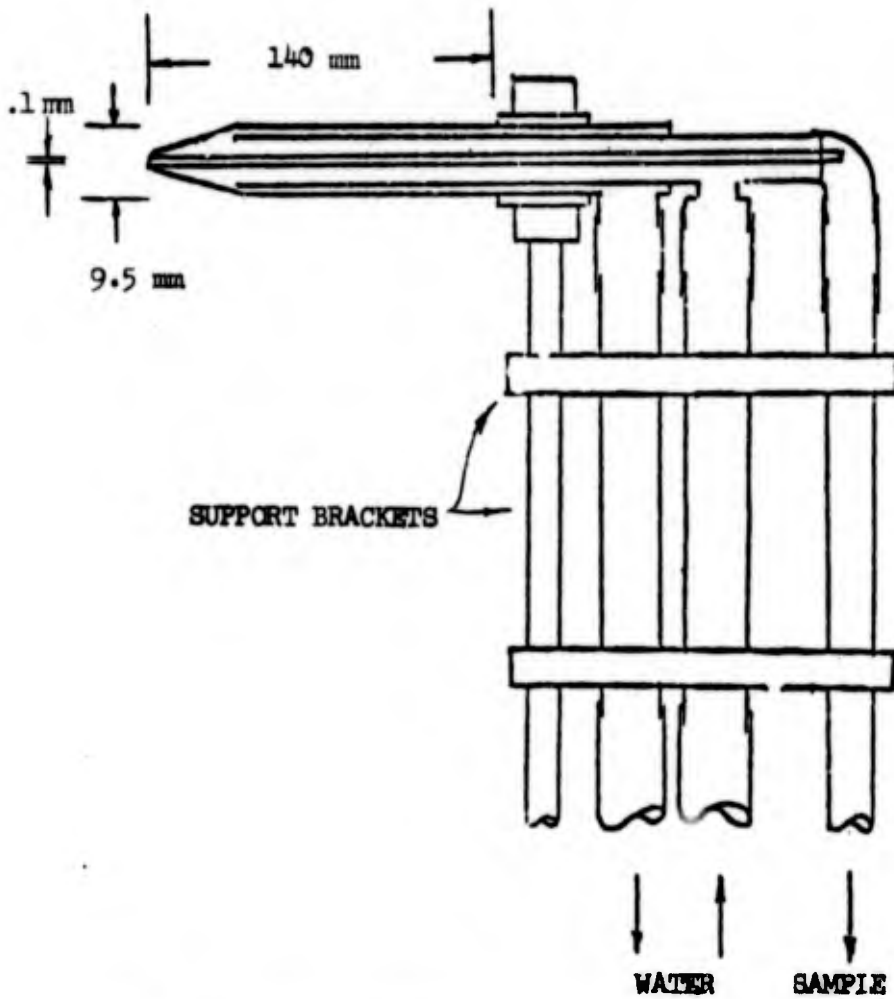


FIGURE 6. Watercooled quartz probe.

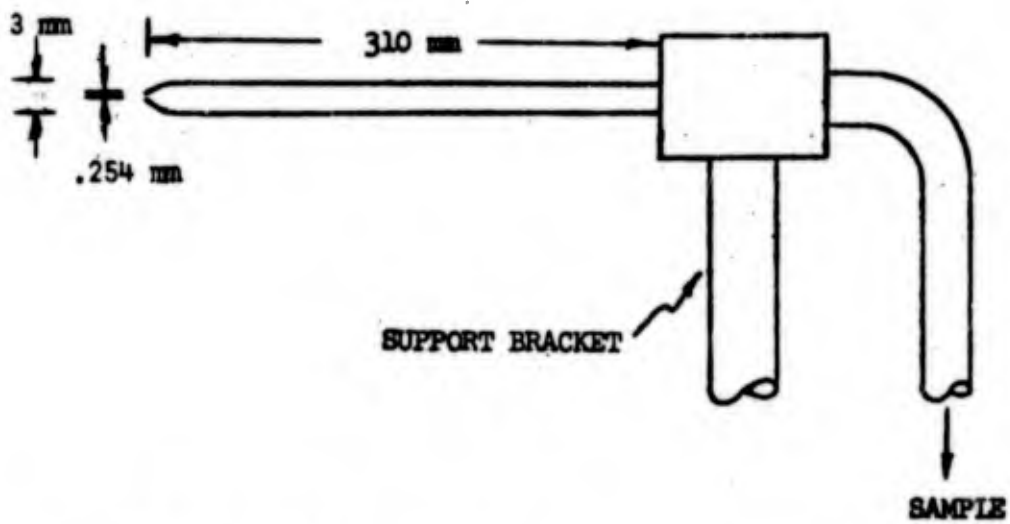


FIGURE 7. Uncooled quartz probe.

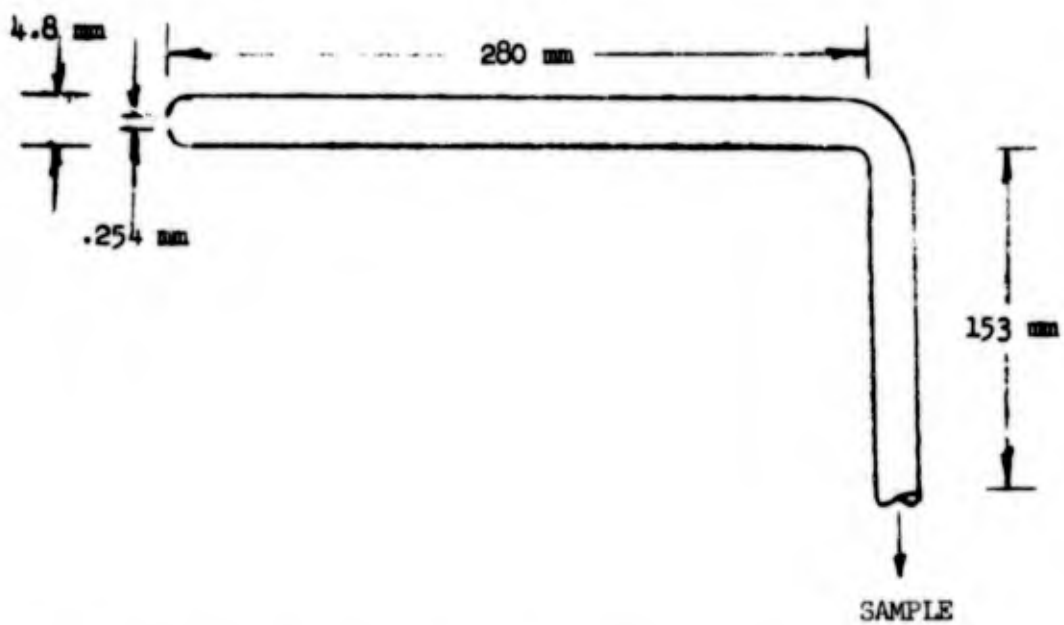


FIGURE 8. Uncooled stainless steel probe.

utilized only in conjunction with the opposed jet stabilized flame, was fabricated by drilling an orifice in a cap welded on the end of a section of stainless steel tubing. The physical dimensions and operating pressures of these probes are summarized in Table 1.

TABLE 1. Sampling Probes

Probe	Mat'l	Cooling	Outside Dia.(mm)	Inside Dia.(mm)	Length (mm)	Orifice Size (mm)	Sample line Pressure (torr)	NO <sub>x</sub> Analyzer Reaction Chamber Pressure (torr)
1a	SS-304	water	4.8	0.97	241	.254	10-40	4.0
1b	SS-304	water	4.8	0.97	241	.152	10-40	4.0
2	Q	water	9.5	0.5	140	.1	10-40	4.0
3	Q	none	3.0	1.0	310	.254	10-40	3.5
4	SS-304	none	4.8	2.8	280	.254	10-40	3.5

#### Analysis for NO<sub>x</sub>, NO, and NO<sub>2</sub>

The anticipated composition of the sample gases required instrumentation capable of measuring accurately the very low NO and NO<sub>2</sub> concentrations expected in these systems, less than 100 ppm. The optimum analyzer for this purpose was found to be a laboratory built chemiluminescent nitric oxide detector<sup>(6)</sup> modified for the additional analysis of total NO<sub>x</sub>. This analyzer operates by measuring the light emitted during the chemiluminescent reaction between ozone and NO. To measure concentrations of NO<sub>2</sub>, therefore, it was necessary to first convert this component to NO. This conversion was accomplished catalytically using heated molybdenum to promote the dissociation of NO<sub>2</sub> to NO.<sup>(7,8)</sup> The sample gases were passed through a 900 mm section of 6.3 mm O.D. molybdenum tubing heated to 500° C, the

$\text{NO}_2$  present was converted to  $\text{NO}$ , and a measurement of total  $\text{NO}_x$  was obtained.  $\text{NO}$  concentrations were obtained by bypassing the converter, concentrations of  $\text{NO}_2$  being determined by difference.

The intensity of light detected by the photomultiplier from the chemiluminescent reaction between  $\text{NO}$  and ozone is proportional to the reaction chamber pressure. Therefore, a constant reaction chamber pressure is required to maintain a single calibration. Because of the change in sample gas properties across the converter (density and pressure), the usual capillary could not be used and reaction chamber inlet valves were used to hold the chamber pressure constant.

## RESULTS

### Turbulent Diffusion Flame

The tip of the turbulent diffusion flame was approximately at an axial distance of four to six inches from the injector with a maximum width of about 0.8 inches diameter. The region inside this flame envelope was fuel rich as verified by  $\text{CO}$  measurements ( $> 1\%$   $\text{CO}$  at 4 inches). It should be noted that because of the shorter length of the watercooled quartz probe, it could not be extended into the combustion system more than four inches downstream from the nozzle, making it impossible to sample in the fuel rich flame interior region.

A comparison of the data for the first three types of probes is shown as a centerline distribution of  $[\text{NO}]$ ,  $[\text{NO}_x]$ , and  $[\text{NO}_2]$  in Figure 9. The plot shows very little difference in the data for the three probes in the post flame gases with the most significant differences in the flame interior. However, because of the difficulty in precisely positioning the probes and because the concentration differences are relatively small,

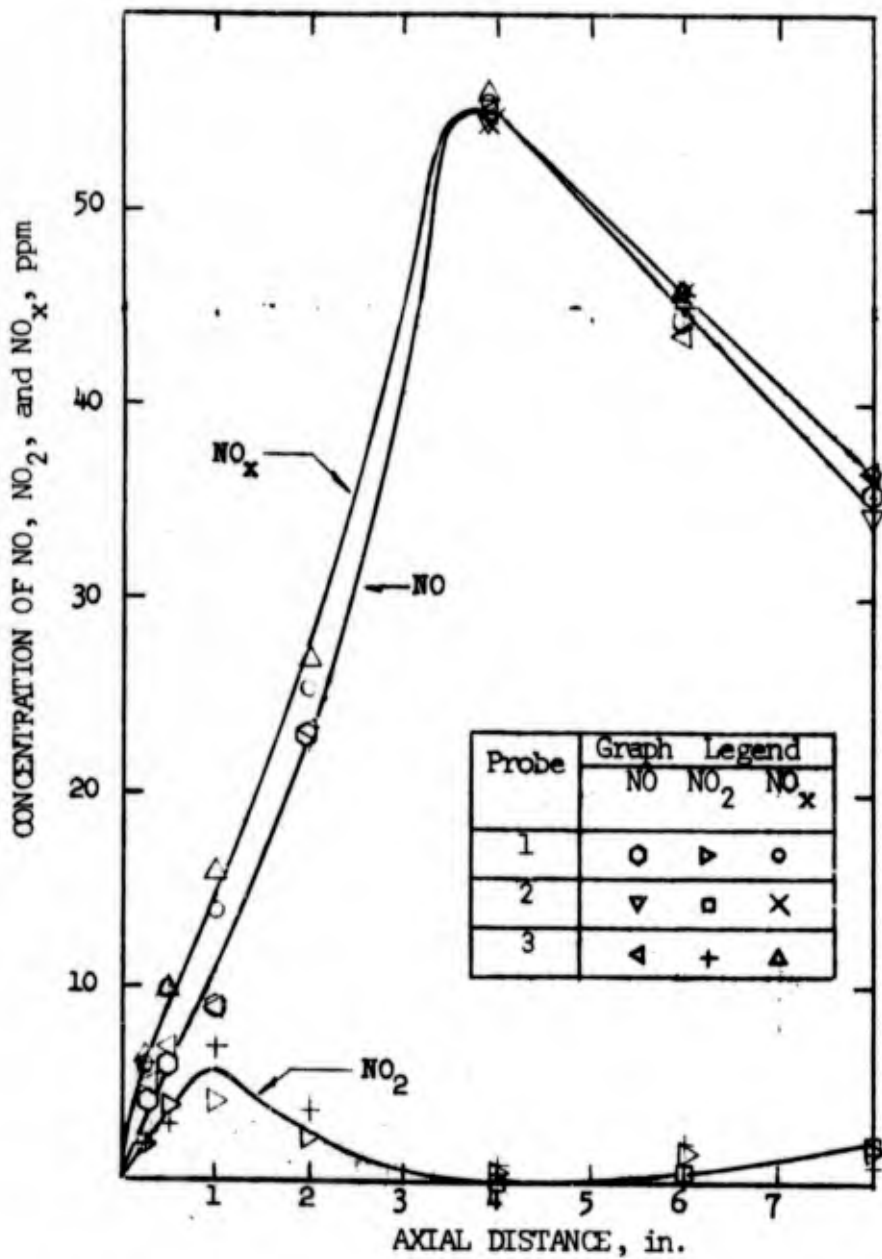


FIGURE 9. Centerline axial distributions of NO, NO<sub>2</sub>, and NO<sub>x</sub> in the simple turbulent diffusion flame.

less than 1.5 ppm, we felt justified in drawing a single curve through each of the sets of data points for NO, NO<sub>2</sub>, and total NO<sub>x</sub>. The radial distributions at an axial location 203 mm downstream from the injector, Figure 10, are typical of the radial distributions obtained. Again it was believed that a single curve through each set of data points could be justified.

#### Opposed Jet Stabilized Flame

Results from the opposed jet study were somewhat surprising because, unlike the turbulent diffusion flame data, noticeable probe effects were observed, the uncooled probes showing a substantially higher fraction of NO. Figure 11 is a graph of the NO and NO<sub>x</sub> concentrations at an axial distance 64 mm from the combustor exit. Axial distributions at a radial location 8.3 mm from the combustor centerline are presented in Figure 12. Because of probe positioning limitations, inlet air humidity variations, and the relatively small differences in concentrations measured by the four different probes ( 2 ppm maximum difference), a single line was plotted through the total NO<sub>x</sub> data. On the other hand, the NO values measured with the cooled and uncooled microprobes were so different as to warrant a separate curve for NO for each of the two cooling configurations. It should be noted that total NO<sub>x</sub> trends agree extremely well with the NO values calculated by Samuelson et al.<sup>(9)</sup>

#### Transfer and Analytical System

The transfer and analytical system was also tested to determine if it could be a significant source of error in the NO<sub>x</sub> measurements.

Prepared gases containing 40 ppm NO in various combinations of N<sub>2</sub>, O<sub>2</sub>, and CO were passed through the sampling and analytical system to see if there was oxidation of NO to NO<sub>2</sub>. Next, a 62 ppm nitrogen dioxide

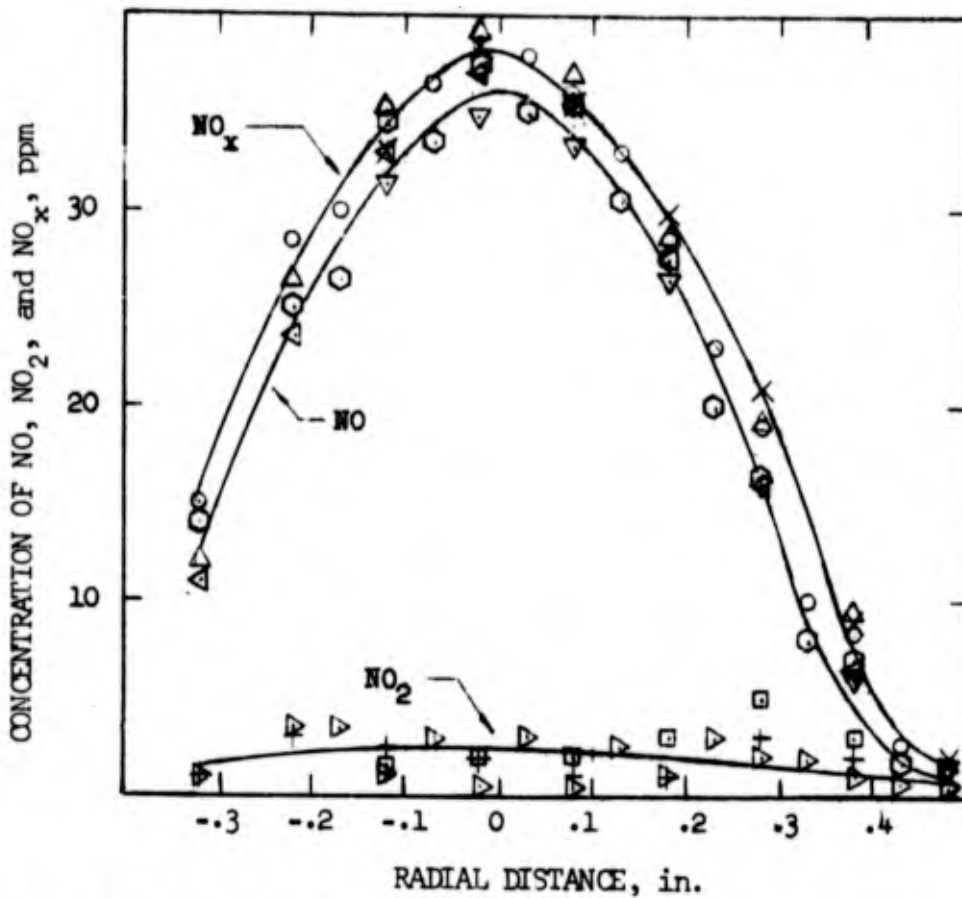


FIGURE 10. Radial distributions of NO, NO<sub>2</sub>, and NO<sub>x</sub> in the turbulent diffusion flame at an axial distance 8 in. from the injector. See Figure 9 for graph legend.

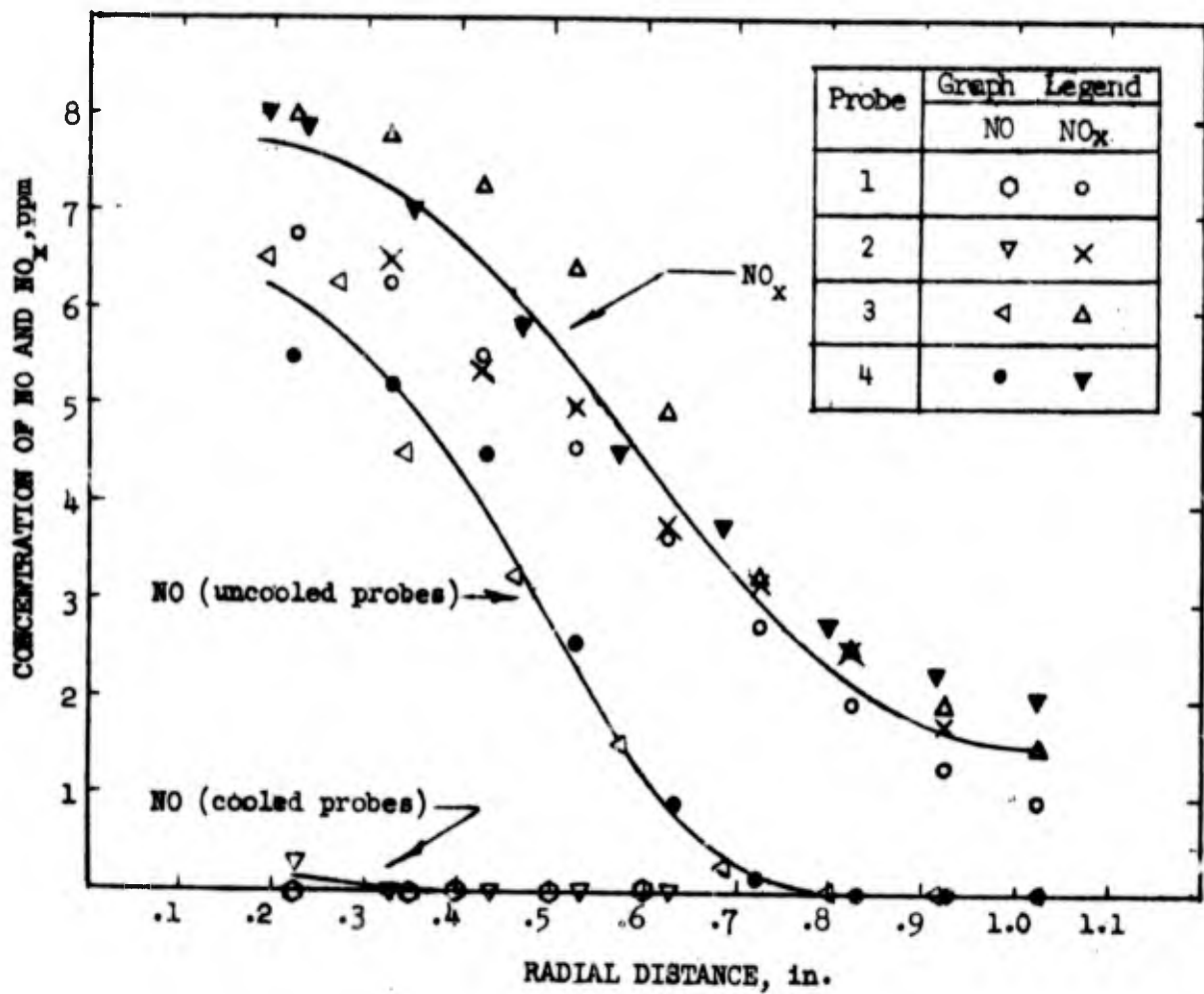


FIGURE 11. Radial distributions of NO and NO<sub>x</sub> in the opposed jet system at an axial location 2.5 in. from the combustor exit.  $\phi = .81$ .

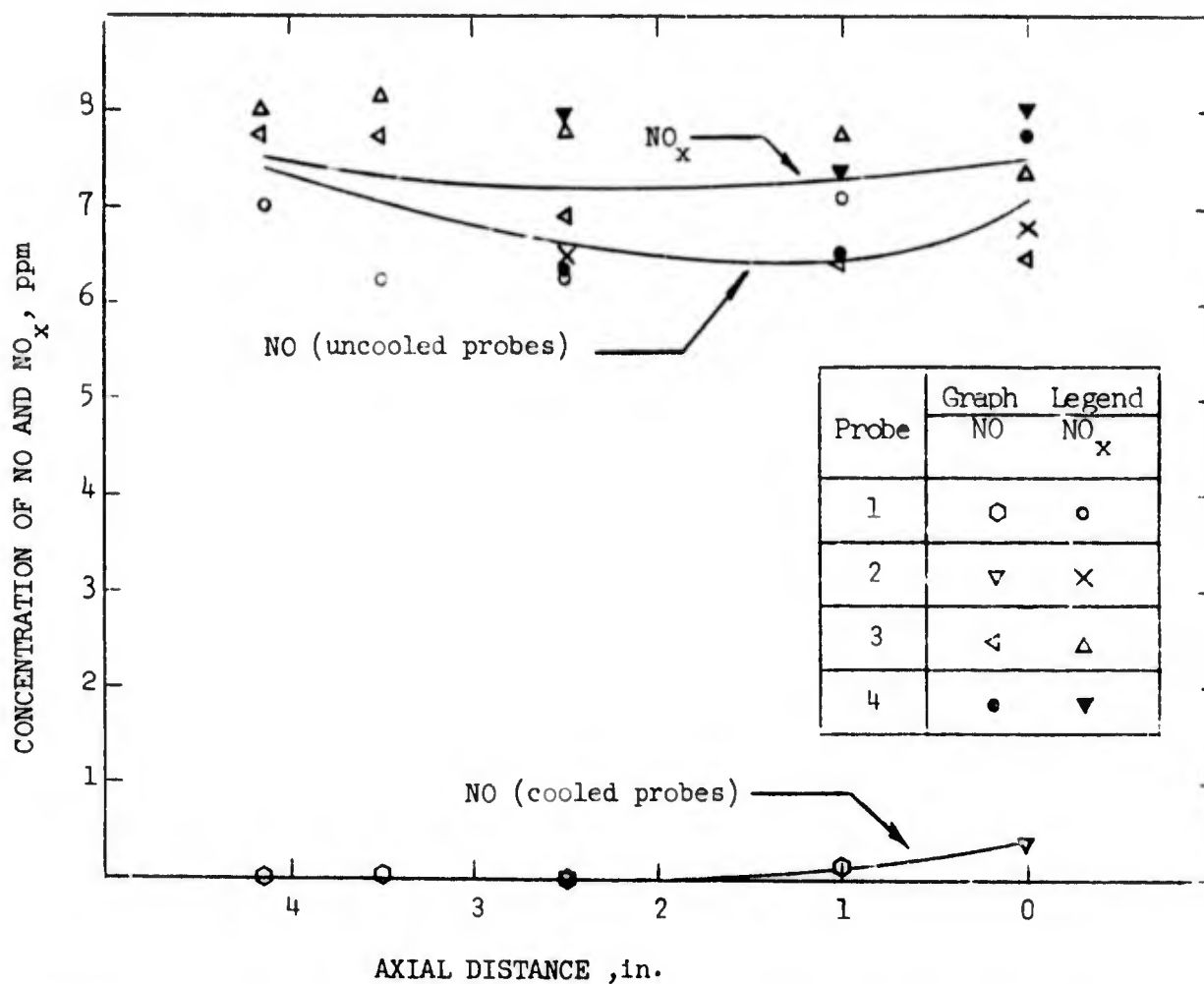


FIGURE 12. Axial distributions of NO and NO<sub>x</sub> in the opposed jet flame at a radial distance of .325 inches from the combustor centerline.  $\phi = .81$ .

in nitrogen calibration gas was pumped through the system to check for decomposition. Neither conversion was observed. This did not rule out, however, transfer and analytical system effects with actual products of combustion which could include hydrocarbons, hydrogen, and other reactive species in addition to NO, N<sub>2</sub>, CO, and O<sub>2</sub>. To eliminate this possibility, products of combustion were sampled from a fixed combustor location while altering the sample line pressure which is normally approximately 30 torr. It was felt that by varying the pressure from 30 to 300 torr, the residence time and collision rate would be sufficiently altered to cause any sample system effects to become apparent. Since no such effects were noted, it was concluded that the transfer and analytical system was not a source of error in the gas analysis.

#### DISCUSSION

All probes yielded similar results for total NO<sub>x</sub> concentrations in both flame systems and therefore any of these probes may be used satisfactorily to sample for the sum of NO and NO<sub>2</sub> in these systems under similar conditions. On the other hand, the type of probe which may be utilized to quantify concentrations of NO and NO<sub>2</sub> depends on the flame system under investigation. In the turbulent diffusion flame, neither cooling configuration or probe material significantly affected measured NO values. For the opposed jet stabilized flame, probe material had no effect while cooling configuration had a substantial influence on measured NO.

This apparent contradiction in results can be reconciled by a more detailed examination of the two systems. The maximum temperature of the premixed opposed jet stabilized flame was lower than that of the

turbulent diffusion flame; however, the opposed jet flame was much longer and had a much larger heat release rate thus allowing greater heat transfer to the probe interior (uncooled probes) as was visually observed. The uncooled probes, therefore, in the case of the opposed jet flame, heated up sufficiently to allow reaction in the probe. This phenomenon was not observed in the turbulent diffusion flame because the hot spots lacked great enough surface area and the remainder of the probe failed to reach the catalytic thermal ignition point.

High temperature stainless steel is a known catalyst for the reduction of  $\text{NO}_2$  to  $\text{NO}$ .<sup>(6)</sup> Thus, the uncooled stainless steel probe would not be expected to yield correct values for  $\text{NO}$  or  $\text{NO}_2$  unless the walls are not heated above the catalytic ignition temperature ( $\sim 500^\circ\text{K}$ ) as was probably the case with the turbulent diffusion flame. The coincidence of the uncooled quartz and uncooled stainless steel probe data would indicate that high temperature quartz is also catalytic for the reduction of  $\text{NO}_2$  to  $\text{NO}$ . It may be concluded, therefore, that cooled probes offer the best chance for success when sampling for  $\text{NO}$  and  $\text{NO}_2$ .

England, et al.<sup>(5)</sup> reported substantial differences in measured  $[\text{NO}_2]$  between cooled quartz and stainless steel probes and between uncooled quartz and stainless steel probes at equivalence ratios greater than 0.7. The current study did not substantiate their findings. Even in the extremely fuel rich regions of the turbulent diffusion flame, no substantial differences between probes were observed. One suspects that difficult sampling conditions might account for some of the differences noted by England et al.; their probes were not designed for aerodynamic quenching and operated at pressures close to one atmosphere.

An interesting byproduct of this experiment is the confirmation of the existence of significant concentrations of nitrogen dioxide in the emissions of typical flame systems. Surprisingly,  $\text{NO}_2$  comprises virtually 100% of the total  $\text{NO}_x$  in the opposed jet stabilized flame system, and as much as 40% in the fuel rich region of the turbulent diffusion flame. This is potentially a very important result and merits further investigation, especially into the kinetics of formation of the  $\text{NO}_2$ .

#### SUMMARY AND CONCLUSIONS

A premixed opposed jet stabilized flame and a simple turbulent diffusion flame were used to study  $\text{NO}$  and  $\text{NO}_2$  measurement techniques. Cooled and uncooled quartz and cooled and uncooled stainless steel sampling probes with tips designed for aerodynamic quenching were used. Gas samples were analyzed using a laboratory built chemiluminescent  $\text{NO}$  detector modified for measurement of total  $\text{NO}_x$ .

No appreciable differences between any of these probes were observed when measuring for total  $\text{NO}_x$ . Cooling configuration and flame system were critical, however, when measuring  $\text{NO}$  and  $\text{NO}_2$ . Therefore, in general, only cooled probes should be used when trying to quantify  $\text{NO}$  and  $\text{NO}_2$  in combustion systems.

Surprisingly large concentrations of  $\text{NO}_2$  were observed in both flame systems;  $\text{NO}_2$  comprising virtually 100% of the total  $\text{NO}_x$  in the opposed jet stabilized flame system, and as much as 40% in the fuel rich region of the turbulent diffusion flame.

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