Interagency Nitric Oxide Measurement Investigation: AEDC Results for Phase III
(Comparison of Optical and Probe Measurements of Nitric Oxide Concentration in Combustors)

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As part of the continuing investigation to determine the cause of differences that were previously found to exist between nitric oxide (NO) concentration measured with conventional sample extraction-gas analyzer techniques and with an ultra-violet (UV) spectroscopic technique, an experimental program was undertaken at United Technologies Research Center (UTRC) Facility, East Hartford, Connecticut. The purpose of Phase III of this program...
was to measure NO concentration on three successively more complicated combustion systems using both optical and probe techniques. The results of all measurements, both probe and optical, were compared and analyzed. Generally, the NO concentrations determined by the optical method were no larger than 30 percent above the values obtained with probes for a methane/air flat-flame burner, a propane/air swirl combustor, and a liquid-fueled simulated jet engine combustor. Close examination of the data revealed that probe results were influenced by some chemical reaction. The probes were designed for subsonic, atmospheric pressure flows, and arguments are presented to show that the agreement found in these experiments need not be expected in near sonic or supersonic flow using the same probe designs.
PREFACE

The work reported herein was conducted by the Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), at the request of the Air Force Engineering and Service Center, Tyndall Air Force Base, Florida. The results of the research were obtained by ARO, Inc., AEDC Group (a Sverdrup Corporation Company), operating contractor for the AEDC, AFSC, Arnold Air Force Station, Tennessee, under ARO Project Number P341-02. The data analysis was completed on October 1, 1979 and the manuscript was submitted for publication on May 1, 1980. The Air Force Project Managers were Capt. Harvey Clewell of Tyndall Air Force Base, and E. L. Hiveley, Directorate of Technology, AEDC. The experimental phase was conducted at the United Technologies Research Center (UTRC) Facility in East Hartford, Connecticut.

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1.0 INTRODUCTION

Differences as large as 500 percent between measurements of nitric oxide (NO) emissions from combustion sources using conventional sample extractor techniques and those using an in situ ultraviolet (UV)-absorption (optical) technique have been reported (Refs. 1, 2, 3, 4, and 5). The Federal Aviation Administration (FAA) is directing an interagency-sponsored program to determine the cause of the differences found between the measurements using the two techniques. The United Technologies Research Center (UTRC) is the prime contractor for the Interagency NO Investigation Program, which consists of three major tasks. Task 1 concerns the development of calibration techniques for the optical measurement system, Task 2 emphasizes determination of the relevant chemistry occurring in the sample extraction and in the transfer lines to the NO measurement instrumentation, and Task 3 includes both optical and probe sampling on three progressively more complicated combustion systems. The Arnold Engineering Development Center (AEDC) role in this program is to (1) provide assistance to the FAA and UTRC with regard to the original computer model for the NO resonance absorption optical technique and (2) to participate in the experimental phases of Tasks 1 and 3.

The optical method employed in the previous measurements (e.g., Refs. 1 through 5) was a resonance line absorption technique. In this technique, the absorption by a gaseous medium containing NO of NO \( \gamma \)-band radiation produced by a discharge lamp containing a mixture of \( \text{N}_2 \), \( \text{O}_2 \), and Ar is measured and related through a theoretical line-by-line radiative transfer model to the NO number density. The interagency program was designed to investigate all aspects of the use of this optical technique and to examine thoroughly probe designs and possible chemical reactions which might affect the probe sampling measurements.

The calibration phase of the program (Task 1) has been completed, and the results are reported by UTRC in Ref. 6 and by AEDC in Ref. 7. Essentially, the results of Task 1 are as follows:

1. Discrepancies were found by UTRC personnel in the theory used in the original AEDC computer model, and some coding errors were also found in the computer code supplied to UTRC by AEDC. The effect on previously reported results could not be assessed directly and re-examination of the model was necessary.

2. The model was corrected, and AEDC and UTRC now use slightly different versions, although the two models are basically the same.
3. A necessary parameter, the collision-broadening parameter, had to be redetermined as a result of the error in the original theory. UTRC determined the parameter experimentally from the observed broadening of resolved lines as a function of pressure and then inferred a band oscillator strength. AEDC determined the parameter by correlation of measured transmittance at low resolution with model results using literature values for the oscillator strength. The UTRC model used with the UTRC parameters and the AEDC model used with the AEDC parameters yield the same transmittance for several test cases considered.

4. Measured transmittances through the flow above a lean H₂/O₂/Ar flat-flame burner seeded with NO, and the transmittance predicted by the model for several values of temperature and seed flow agreed within about 20 percent. Similar results were obtained by comparing the measured transmittances through the flow from an electrically heated quartz bed heater consisting of N₂ and seeded NO, or Ar and seeded NO, to the model predicted transmittances. Most of the uncertainty was attributed to the probe measurements of temperature and NO concentration radial profiles, which were essential inputs to the computer radiative transfer code because of the inhomogeneous path provided by the calibration sources. These calibration sources were designed to provide exhaust gas compositions in which no reactions between NO and other species could be expected. To that end, the program appeared to be very successful and the calibration phase was deemed to be satisfactory.

The sample extraction and analysis phase of Task 2 is reported in Ref. 8. In this phase several probe designs are used in a methane/air flame, a propane/air swirl combustor, and a jet fuel/air combustor to measure NO and NOₓ concentrations.

Results from Task 2 are as follows:

1. Cooled probes in which the temperature is reduced rapidly to less than 1,000°K in about 1 to 2 msec do not disturb the NO concentration in sampling hydrocarbon exhaust gases at temperatures up to 2,000°K for equivalence ratios between 0.8 and 1.2.

2. Uncooled or poorly cooled stainless-steel probes exhibit destruction of NO at stoichiometric and larger equivalence ratios; no destruction was observed for an equivalence ratio of 0.8.
3. No advantage was found in aerodynamic over purely convection cooling within the probe.

During the final phase of Task 3, probe measurements and UV resonance absorption measurements of NO concentration were made on the effluents from the three hydrocarbon combustors. These combustors are supposed to represent successively more complex combustion processes, to satisfy the overall goal of determining whether the differences reported previously in NO concentration measured by probe sample extraction and optical methods in jet engine exhausts were real, and, if so, to identify the cause. The UV resonance absorption measurements were made by both UTRC and AEDC. In addition, an IR absorption technique to measure NO concentration was employed by representatives of the Ford-Philco Corp. The UTRC and Ford-Philco measurements and analysis are reported in Ref. 9. The AEDC portion of Task 3 is reported herein.

The three hydrocarbon combustors selected were (Ref. 8):

1. Flat-flame burner (FFB) burning methane (CH$_4$) with a mixture of oxygen (O$_2$) and nitrogen (N$_2$).

2. Swirl combustor after the model adopted by the International Flame Research Foundation (IFRF) burning propane (C$_3$H$_8$) with air.

3. Jet engine combustor, a modification of the standard Pratt and Whitney Model FT-12 Combustor, burning Jet A fuel with air.

The FFB burning methane at lean, stoichiometric, and rich equivalence ratios is meant to provide the extension from the lean H$_2$/O$_2$ FFB to a combustion situation where free radicals, hydrocarbon fragments, and free hydrogen are available to react with the NO. The propane-fueled IFRF combustor offers slightly more complex chemistry, and the FT-12 combustion products should be similar to the final composition of jet engine exhausts. The IFRF and FT-12 combustors exhausted into a large plenum chamber where the velocity was on the order of a few feet per second. This latter factor represents the major difference in the combustor exhausts employed in this study and jet engine exhausts in which the velocities are much greater.

The AEDC measurements were made under similar conditions of operation of the combustors as those made by UTRC and Philco-Ford. The combustors were operated by UTRC, and AEDC was supplied a set of probe-measured temperature and NO, NO$_x$ concentration profile data along the optical path. These data are required in the analysis and
reduction of the optical data because of the nonhomogeneity of the temperature and NO concentration along the single observation path, and are included herein. The optical system will be described briefly, as will the UV resonance absorption technique and the data reduction procedure. The results of the data reduction will be presented and discussed and conclusions will be presented.

2.0 COMBUSTOR FACILITIES

The combustor facilities, probe designs, operation of facilities, and probe measurements were the responsibility of UTRC and are fully described in Ref. 8. For completeness the facilities will be briefly discussed here, and the temperature and NO concentration profiles measured by UTRC are presented since these data are integral to the determination of the NO concentration by the optical method.

2.1 FLAT-FLAME BURNER

The CH$_4$/O$_2$/N$_2$ flat-flame burner had interior dimensions of 17.5 by 9.2 cm (see Fig. 1). A surrounding buffer zone (area 76 cm$^2$) contained a methane flame (Fig. 1) which served to isolate the inner burner flame from the ambient atmosphere.

The gas sampling of the flat-flame burner was accomplished in the main flow 2 cm from the burner face by stainless-steel-tipped, water-cooled probes, and the samples were analyzed using conventional gas analyzer instrumentation. The probe-measured NO concentration profiles for the flat-flame burner are given in Figs. 2, 3, and 4 at equivalence ratios ($\phi$) of 0.8, 1.0, and 1.2, respectively. The profiles are shown normalized to seed values determined by a gas metering system.

The exhaust gas temperature profiles were obtained using a butt-welded, Ir 60-percent/Ir 40-percent Rh thermocouple coated with a mixture of yttrium and beryllium oxides. The temperature profiles are given in Figs. 5, 6, and 7 for the three equivalence ratios. The optical axis coincided with the placement of the probes.

2.2 IFRF SWIRL COMBUSTOR

The IFRF combustor (Fig. 8) is a model of those burners described in Ref. 10 and consists of a central fuel nozzle and annular air supply. The operation of the combustor is further described in Ref. 8. The IFRF combustor was operated with propane (C$_3$H$_8$) and air at equivalence ratios of 0.8, 1.0, and 1.2.
The gas sampling of the IFRF combustor was accomplished by a stainless-steel water-cooled orifice probe located 87.5 cm downstream of the combustor exit (Ref. 7). Probe-measured NO concentration profiles are given on Figs. 9, 10, and 11 for equivalence ratios of 0.8, 1.0, and 1.2, respectively.

The exhaust gas temperature profiles were obtained using a water-cooled, double-shielded, aspirated thermocouple probe with a bead made of Pt/Pt 13-percent Rh. Further description of the probe and the radiation and conduction corrections are given in Ref. 8. The temperature profiles were made in the same plane (87.5 cm downstream) of the combustor exhaust as the concentration measurements and are given for the three equivalence ratios on Figs. 12, 13, and 14.

### 2.3 FT-12 COMBUSTOR

A modified FT-12 engine combustor can 29.5 cm in length (11.5 cm shorter than original) and 13.0 cm in diameter is shown in Fig. 15. The combustor was operated at equivalence ratios of 0.14, 0.19, and 0.20, corresponding to simulated conditions of idle, cruise, and maximum continuous power, respectively, using Jet A fuel.

The gas sampling of the FT-12 combustor was accomplished using a stainless-steel orifice water-cooled probe (Ref. 7). The probe axis was 78 cm downstream from the FT-12 combustor exit. The probe-determined NO concentration profiles are shown in Figs. 16, 17, and 18 and the exhaust gas temperature profiles are shown in Figs. 19, 20, and 21 for the idle, cruise, and maximum continuous simulated throttle positions.

### 2.4 TEST SECTION

A test section (or plenum chamber) was used with the IFRF and FT-12 combustors and is shown schematically in Fig. 22. It consists of a water-cooled, double-walled chamber, 50 cm in diameter (ID) and 150 cm long. The optical access was an open port approximately 2.5 cm in diameter located at the center of the third window from the right as indicated in Fig. 22. The optical axis coincided with the axis of both the sample probe and the thermocouple probe for both the IFRF and FT-12 combustor operations.
3.0 OPTICAL METHOD

3.1 UV RESONANCE ABSORPTION TECHNIQUE

The UV resonance spectral line absorption technique has been employed frequently to make species number density measurements in an absorbing medium (e.g., Ref. 11). The method is here applied in a manner developed at AEDC (e.g., Refs. 1 through 5) for the NO molecule. The apparatus and data treatment are very similar to the previous UTRC measurements reported in Ref. 7, although for each measurement configuration the data treatment will vary to some extent.

The technique as employed here can be illustrated with the help of Fig. 23. The spectral intensity of the (0,0) band of the \( \gamma \)-system of NO emitted from an electrical discharge at low pressure is first measured using a low resolution spectrometer with no absorbing gas in the optical path. This spectrum provides a reference. Then the spectral transmission through the absorbing gas is measured, and the ratio of the signals (transmittance) at the same wavelength is obtained. The spectral features of the (0,0) NO \( \gamma \)-band (see Fig. 23) make it convenient to measure the transmittance at the maximum intensity point, the second bandhead, although any other wavelength (e.g., the first bandhead) could have been chosen. A line-by-line radiative transfer mode is then used to calculate the transmittance along the path for a known temperature, pressure, and NO concentration profile.

At this point some additional explanation is in order. If the absorbing path is homogeneous in temperature, pressure, and NO concentration, then it is only necessary to repeat the calculation using different values of the NO concentration until the calculated transmittance matches the measured value. This procedure may produce a calibration curve of NO concentration (or number density), or the numerical iteration may be done automatically by the computer.

However, if the optical path is not homogeneous, the temperature and pressure profiles are required and the technique can only produce some weighted average NO number density. If additional knowledge of the shape of the NO distribution along the path is available (e.g., from probe sampling), then the radiative transfer calculation can proceed with a normalized NO concentration and the normalization factor can be iterated upon until agreement between measured and calculated second bandhead transmittance is obtained. A third and more desirable scenario is encountered when several measurements can be made at one axial plane and the cross section of the plume is circular, or at least symmetric. Then a spatial inversion can be employed to determine radial variations of the NO concentration (e.g., Refs. 2, 3, 4 and 5).
In the case of the UTRC measurements, a nonhomogeneous path was always encountered, as shown by the temperature and NO concentration profile data of the previous section. The static pressure was assumed constant at atmospheric pressure for the UTRC combustors. The NO concentration profiles determined by the sampling method were normalized to the centerline value, and the centerline value was varied to obtain calibration curves. The necessity for making the assumption that the probe-determined NO concentration profile is correct is the weakest link in this procedure.

The physics employed in the current model has been adequately described in Ref. 7. The voight line profile-broadening coefficients for N₂ and CO₂ foreign gas broadeners as given in Ref. 7 were used and the relation given in Eq. (14) of Ref. 7 was used to determine the coefficients for the other major species, O₂ and H₂O. The radiative transfer calculations were made by the "marching procedure" outlined in Section 3.3.1 of Ref. 7, rather than by assuming Beer's Law as is done in the UTRC procedure (Refs. 6 and 9).

The method employed in previous work to correct the reference intensity in case of instrument drift or response, window fogging, and other factors is also employed here. The (2,2) band of the NO γ-system, which is evident in the spectral trace shown in Fig. 23, should not absorb at the temperatures encountered in this study. In fact, at 2,000°K less than 1 percent of the ground state NO molecules will be in the v = 2 vibrational state. Thus, any apparent reduced signal at the peak of the (2,2) band can be interpreted as an experimental effect not attributable to NO absorption. The ratio of this signal to that of the reference signal then serves as a correction factor to the measured transmittance at the second bandhead of the (0,0) transition.

### 3.2 APPARATUS AND DATA ACQUISITION

The AEDC UV Resonance Absorption System used for the UTRC combustor measurements consisted of a capillary discharge lamp UV source, a 1/2-m Jarrell-Ash grating (2,380 grooves/mm) spectrometer employing a Hamamatsu R166UH photomultiplier detector, associated signal-conditioning electronics, a Hewlett-Packard 5480B signal averager, and a Honeywell 5600C fm tape recorder. The system is shown schematically in Fig. 24.

Data were obtained at UTRC by scanning the spectrum 32 times and by averaging the spectrum using the Hewlett-Packard 5480B signal averager. The averaged spectrum was then recorded on fm tape and on an X-Y plotter. A reference spectrum was obtained before and after each test condition on the UTRC combustor systems, and several data points at the different operating conditions given in Section 4.0 were obtained. Typical spectral data for FFB, IFRF, and FT-12 combustors are given in Figs. 25, 26, and 27 respectively.
3.3 DATA TREATMENT

The calibration curves for the three combustors at the various conditions of operation determined by the calculational procedure described in Section 3.1 are given in Figs. 28a, b, and c. The abscissa is the transmittance, and the ordinate is the predicted centerline concentration in parts per million (ppm). The data reduction is then used to determine the measured transmittance and to determine the centerline concentration from the calibration curves.

Reduction of the experimental data to transmittance was complicated by a continuum absorption over all [(3,4) (0,0), (1,1), (2,2)] the NO \( \gamma \)-bands scanned when the FFB, FT-12, or IFRF combustors were operated as shown in Figs. 25, 26, and 27. The correction for the continuum absorption was made to the data by use of the (2,2) band apparent signal reduction, as described in Section 3.1. This correction factor was determined from the spectral scan taken after the combustors were started but before the seed flow was started. Thus, a reference (hot) trace was established which should be identical to the original (cold) reference.

Only a small correction was required for the FFB data because of continuum absorption, and the hot reference could be made to reproduce the cold reference.

A continuum absorption (20 percent) was observed in the IFRF combustor exhaust at onset of combustion. The (2,2) band of the NO \( \gamma \)-system was used to determine the correction factor and was applied to the second bandhead of the (0,0) transition. The correction factor did not re-establish the hot reference over the entire (0,0) band as in the case of the FFB. The (0,0) \( \gamma \)-band, after correction, resulted in approximately 95 percent transmittance at the combustor condition. This 95-percent transmittance relates to 50 ppm of NO at centerline because of the combustor production and compares to 45 ppm of NO measured by the probe at the same condition. The correction factor was thus carried through on all data points by accounting for the combustor production in determining the hot reference. The final transmittance from which the NO concentration values are reported thus includes the seed plus the combustor production.

The FT-12 combustor exhibited a very strong continuum absorption (approximately 90 percent) when operating at the idle equivalence ratio. The cruise and maximum continuous operating conditions did not show as much extraneous absorption; however, 20 to 25 percent was the rule. The same procedure was used to correct these data that was used for the IFRF combustor data; i.e., the (2,2) band was used to determine the correction factor to re-establish a hot reference trace with account taken of the combustor production of NO.
However, when nitric oxide was seeded into the combustor, the absorption at the (0,0) transition increased in a normal fashion but the absorption at the (1,1) and (2,2) transitions decreased relative to the hot reference (see Fig. 26). Again the (2,2) transition was used to re-adjust the reference to establish the final transmittance at the (0,0) second bandhead to be used in determining the NO concentration level. This procedure should be satisfactory if the extraneous absorption remains constant over the entire (0,0) and (2,2) bands.

4.0 RESULTS

The values of NO concentration at the stream centerline obtained from the measured NO $\gamma$-band transmittances, and the NO and NO$_x$ concentrations obtained from probe sampling measurements are presented in Tables 1, 2, and 3 for the FFB, IFRF, and FT-12 combustors, respectively. The input seed values of NO concentration, and the values of NO and NO$_x$ concentration produced by the combustion process as measured by the probe method are also given in Tables 1, 2, and 3 for the three combustors. The seed plus flame production values will hereafter be referred to as the input values and will be used as a reference value for comparison purposes. The procedure described in Section 3.0 was used to obtain the optically measured NO concentration values. The optically determined centerline NO concentration, and the probe-determined centerline NO and NO$_x$ concentrations raised to the input values are plotted versus equivalence ratios for the FFB, IFRF, and FT-12 combustors, respectively, in Figs. 29, 30, and 31. These results are discussed for each combustor in the following sections.

4.1 FLAT-FLAME BURNER

Table 1 shows that optically and probe-measured centerline NO concentrations on the FFB differ by no more than 26 percent for all the data obtained. However, additional information that may be pertinent to this study is available when the results are examined in detail. The more significant observations are:

1. Ninety-five percent or greater of the total oxides of nitrogen (NO$_x$) were measured as NO in the probe extraction method. This indicates that little, if any, oxidation of NO to NO$_2$ occurred either in the flame, probe, and/or sample line for this combustor source.

2. At the higher equivalence ratios, both the optical and probe measurements show an apparent destruction of NO$_x$ in the flame when compared to the input values of NO concentration. Approximately 60 percent of the NO is destroyed in the
flame at the equivalence ratio of 1.2, whereas the optical and probe measurements agree within 1 percent at this burner condition.

3. Figure 29 shows the ratio of optically measured centerline NO concentration to the input NO concentration and the probe-measured centerline NO concentration to the input as a function of equivalence ratio. The plot shows a difference between the probe-measured NO concentration and the input of approximately 20 percent at an equivalence ratio of 0.8, whereas the optically measured NO concentration agrees within 6 percent with the input at this burner condition. Furthermore, no flame destruction of NOx is indicated by the optical method at the 0.8 equivalence ratio. As the equivalence ratio increases, the measured values of NO concentration by both the optical and probe techniques decrease. The magnitude of the difference in the probe and optical measurements is much smaller at the larger equivalence ratios, and good agreement is evident even though an apparent destruction or loss of NOx is occurring.

4.2 IFRF SWIRL COMBUSTOR

Examination of Table 2 will reveal that the optically and probe-measured centerline NO concentrations taken in the plenum section on the IFRF combustor facility differ by no more than 20 percent. Again there is more information pertinent to this study available when the data are examined in detail.

1. The probe-measured NO concentration for the IFRF combustor shows that 98 percent of the NOx is measured as NO over the range of equivalence ratios from 0.8 to 1.2. As in the FFB, very little NO2 is measured in the probe sample, thus indicating little or no oxidation of NO to NO2 in the flame, probe, or sample line.

2. The optically and probe-measured NO concentrations agree at the equivalence ratio of 0.8, and both measurements agree with the input seed plus flame production. This differs from the probe measurement on the FFB at the 0.8 equivalence ratio where there was an apparent loss of NOx compared to the input NO. It may be important to note that a small, water-cooled, stainless-steel miniprobe was used for the FFB whereas a larger water-cooled orifice-type probe was used for the IFRF combustor. Evidently the chemical reaction occurring at the entrance to these two probes is different.
3. At the higher equivalence ratios (Table 2 and Fig. 30) there appears to be flame
destruction of NO\textsubscript{\text{t}} when compared to the input NO concentrations. Here again,
probe-and optically measured NO concentrations agree within a few percent.

4.3 FT-12 COMBUSTOR

From Table 3 and Fig. 31, it is observed that the total spread between probe-measured
NO\textsubscript{x} concentration and optically measured NO concentration is no more than 30 percent
over the combustor operating range equivalent to engine idle to maximum continuous
operations. Some detailed observations from the data are as follows:

1. The difference in the optically measured NO concentration and the input seed
plus flame production value ranges from -9 percent to 5 percent at the maximum
continuous equivalence ratio (or, an average of ±5.5 percent). This indicates
very little loss in NO or oxidation to NO\textsubscript{x} in the combustion and flow process.

2. The probe-measured NO concentration is significantly less than the probe-
measured NO\textsubscript{x} concentration at all operating equivalence ratios; the difference
(36 percent) is most pronounced at the idle (\(\phi = 0.14\)) condition and becomes
less as the equivalence ratio increases. This result is contrary to that for the FFB
and the IFRF where little difference between NO\textsubscript{x} and NO concentration was
observed.

3. The difference in the probe-measured NO\textsubscript{x} concentration and the input seed plus
flame production value ranges between -37 percent at the idle equivalence ratio
(0.14) to -8 percent for one of the maximum continuous equivalence ratio settings
(see Fig. 31). This result is in disagreement with the observation based on the
optical measurement and indicates some loss of NO\textsubscript{x} within the probe sampling
system. This result, coupled with the conversion of NO to NO\textsubscript{x} within the probe,
is an indication that chemical activity is greater with the liquid-fueled
combustor.

5.0 DISCUSSION

5.1 MEANING OF INTERAGENCY STUDY

The interpretation of the results of this study may be cast in two ways. First, the meaning
of the specific measurements made during the study as they pertain to the technology of the
measurement techniques can be assessed. Second comes consideration of the degree to which
the question regarding disagreement between optical and probe measurements in jet engine exhausts has been answered.

In brief, the accomplishments of the Interagency NO Investigation Program can be summarized as follows:

**Task 1.** The line-by-line radiative transfer model for the (0,0) band of the NO γ-system was thoroughly investigated, errors found were corrected, the model was put on an accurate foundation, and the technique was calibrated within the uncertainties of the probe-measured temperature and NO concentration profiles along the optical path, for temperatures up to about 1,800°K at atmospheric pressure.

**Task 2.** Perturbations on the NO concentration in hydrocarbon flames and combustors result when sampling probe tips are not properly designed for the environment in which they are placed; for example, uncooled stainless-steel probes immersed in low velocity hydrocarbon combustion gases show large errors in NO concentration, whereas several designs of adequately cooled probes give the same concentrations, and the measurement agrees well with input values of NO.

**Task 3.** Optically measured NO concentrations in the low-velocity hydrocarbon combustion exhausts used in the UTRC program agree with the "properly designed" probe-measured values, on the whole, within 30 percent. Upon closer investigation, this 30-percent band reveals that some unexplained chemical activity is taking place, particularly in the case of the liquid-jet-fueled combustor.

Weaknesses of the interagency program also should be pointed out. These include:

**Source Inhomogeneities.** In all four combustion gas sources used — flat-flame burner, flowing gas heater, gaseous-fueled swirl combustor, and liquid-fueled jet engine combustor — the temperature and NO concentration profiles along the optical transmission path were inhomogeneous. This necessitated a zonal approach to the single line of sight measurements in which the absolute temperature profile and the NO concentration profile had to be used in order to calculate the transmittance. In the calibration phase (Task 1) the probe-measured temperature and NO concentration profiles were used to calculate the transmittance by dividing the path into a series of homogeneous zones which approximated the inhomogeneous path. The calculated transmittances were then compared to the measured transmittance. In the combustor measurements (Task 3) the probe-measured NO concentration profile shape was assumed to be correct and was
normalized. The centerline absolute concentration was then varied in the calculation to provide a calibration curve. It is significant to note that in both cases the decision on agreement or disagreement is based in part on the probe measurement of the NO concentration. In other words, the two measurements are not independent. In a more satisfactory experiment the source would have been homogeneous or the profiles would have been axisymmetric and the lateral profile of transmittance could have been inverted to obtain a radial profile of the NO concentration (e.g., Refs. 3, 4, and 5). Then, the independence of the two techniques would have been assured.

Source Parameter Uncertainties. The limiting uncertainty in the calibration phase (Task 1) was in the probe measurements (Refs. 6 and 7) of temperature and NO concentration. The temperature uncertainty resulted from the necessity to correct the thermocouple data for radiation losses. The NO concentration uncertainty (about ±10 percent) arose from the scatter in measurements. Thus, the high temperature calibration data uncertainty was no better than about ±20 percent (Ref. 7).

Probe Design. The probes used in the program were designed for low-subsonic flow application at atmospheric pressure. In most cases, the probes used in the studies in which discrepancies between probe and optical measurements of NO concentration were found (e.g., Refs. 1 and 5) were of the EPA recommended orifice design, similar to the UTRC-designed EPA probe (Ref. 8), but the measurements were taken in supersonic flow. Thus the interagency study has not addressed the probe operation in the flow environment in which most of the discrepancies were originally found. The UTRC emphasis on “properly designed probes” for the flow environment in which they are to be used is well founded, but the program did not investigate what may be expected when a probe is operated outside its design environment.

Combustion Gas Flow Properties. The interagency study adequately addressed the case of the low velocity, equilibrium combustion gas. Transit times between the flame front and the probes were estimated to be on the order of several milliseconds on the FFB to near 100 msec for the IFRF and FT-12 combustor rigs. In jet engines the transit time is more nearly about 1 msec. Also the velocity at jet engine nozzle exits is usually near Mach 1 compared to a few feet per second for the UTRC combustion sources. Thus, the chemistry, as well as the gas dynamics near the probe inlet, may be more different for jet engine exhausts than for the combustor flows used in this program. The presence of a few free radicals in a stagnation zone could significantly alter the chemical reaction taking place.
From the above discussion it may be concluded that some questions are still left unanswered regarding the behavior of probes in the supersonic exhaust of jet engines.

5.2 RE-EXAMINATION OF PREVIOUS DATA

The errors found in the theory (Refs. 6 and 7), coupled with the inability to substantiate some of the data used for determination of the line-broadening parameter (Refs. 12 and 13), throw doubt on the previous measurements of NO concentration in combustor and jet engine exhausts. It is thus necessary to re-examine all the data obtained in the past and determine the NO concentration in each case using the revised model. AEDC is in the process of making these determinations. One case will be given here as an example of what changes might be expected.

The optical data obtained from the exhaust of the F101-GE-100 engine (Ref. 5) represent probably the most accurate so far obtained from a jet engine. Complete lateral profile absorption data were obtained by spatially scanning the exhaust plane about 10 cm downstream of the nozzle exit plane. The data were then inverted to obtain a radial distribution of the NO concentration using the technique described in Refs. 3 and 4. In the original work the optically determined centerline value was larger than the probe-determined value by a factor of about 2.2. In the revised model both the theoretical corrections and the improved radiative transfer procedure described in Ref. 7 were employed. The original and revised results are shown in Fig. 32 for the one engine operating condition (intermediate power) for which probe sampling data were available. It is noted that in this case the centerline concentration was reduced by the new calculation by about 20 percent but disagreement between optical and probe measurements is still about a factor of 1.7. The probe used for these studies was an orifice probe having a 0.2-cm-diam inlet whose diameter rapidly expanded to 0.51 in. The UTRC EPA probe was almost identical — a 0.2-cm-diam inlet with diameter expansion to 0.31 cm, which UTRC believes would not be suited to supersonic flow sampling (Ref. 8).

It is not possible to make blanket statements about other previously published data owing to the uniqueness of each radiative transfer calculation situation.

5.3 STATUS OF THE NO MEASUREMENT PROBLEM

The current interagency investigation has done much to illuminate the optical versus probe measurement problem. The model is now on sound foundation, and it has been shown that results can differ significantly when different probe designs are employed. For three different types of combustion processes, the optically and probe-measured NO concentrations agreed reasonably. However, the gas streams were low-velocity, equilibrium
cases and the probes were "properly" designed for the specific environments. It still remains to determine whether agreement will be the same for a real jet engine exhaust, where a different probe geometry will be required for the near sonic flow situation.

6.0 CONCLUSIONS

The major conclusions to be reached from the AEDC portion of the Task 3 phase of the Interagency NO Investigation are as follows:

1. For three low-velocity hydrocarbon combustors the overall difference between optically measured NO and probe-measured NO\textsubscript{x} concentrations was never more than 30 percent, and the optical measurement was always greater than the probe measurement.

2. Trends in the probe-measured NO and NO\textsubscript{x} concentrations lead to the conclusion that chemical effects are taking place within the probe and sample transfer line.

The main conclusions drawn from the entire program are as follows:

1. The original AEDC theoretical model was in error and a successful revision was made.

2. The model was successfully calibrated using lean, clean flat-flame burner and flowing gas heater sources, but the calibrations were not completely satisfactory because of temperature and NO concentration gradients along the optical path.

3. Different probe designs give different NO concentrations, and probes must be specially designed for each application.

4. For low-velocity hydrocarbon combustion gas streams, optically measured NO concentration and probe-measured NO\textsubscript{x} concentration may be expected to agree within about 30 percent, with the probe results biased to lower values than for the optical method.

5. The final answer to the question of whether probe and optical measurements can be expected to agree in jet engine exhausts, where flow conditions are considerably different than for the UTRC studies, has yet to be found. A final experiment seems warranted in which either a jet engine exhaust, or a good simulation of a jet engine exhaust, is used for the measurements.
REFERENCES


Figure 1. Top view of flat-flame burner and assembly.
Figure 2. Normalized probe-measured nitric oxide concentration profiles across CH₄/O₂/N₂/NO flat flame – φ = 0.8.
Figure 3. Normalized probe-measured nitric oxide concentration profiles across CH₄/O₂/N₂/NO flat flame – φ = 1.0.
Figure 4. Normalized probe-measured nitric oxide concentration profile across CH$_4$/O$_2$/N$_2$/NO flat flame — $\phi = 1.2$. 
Figure 5. Horizontal probe-measured temperature profile across CH₄/O₂/N₂ flat flame — φ = 0.8.

O Thermocouple Temperature Corrected for Radiation
Figure 6. Horizontal probe-measured temperature profile across CH₄/O₂/N₂ flat flame - $\phi = 1.0$. 

O Thermocouple Temperature Corrected for Radiation
Figure 7. Horizontal probe-measured temperature profile across \( \text{CH}_4/\text{O}_2/\text{N}_2 \) flat flame – \( \phi = 1.2 \).
Figure 8. IFRF swirl combustor assembly.
Figure 9. Normalized probe-measured nitric oxide concentration profile across IFRF combustor flame No. 4 — $\phi = 0.8$, swirl 4.
Figure 10. Normalized probe-measured nitric oxide concentration profile across IFRF combustor flame No. 5 — $\phi = 1.0$, swirl 4.
Figure 11. Normalized probe-measured nitric oxide concentration across IFRF combustor flame No. 6 — $\phi = 1.2$, swirl 4.
Figure 12. Probe-measured temperature profile across IFRF combustor flame No. 4 – $\phi = 0.8$. 

- Pt/Pt - 13 percent Rh Aspirated Thermocouple Probe Corrected for Radiation and Conduction
- 0.10-in. Cr/Al Thermocouple
Figure 13. Probe-measured temperature profile across IFRF combustor flame No. 5 – $\phi = 1.0$. 

- Pt/Pt - 13 percent Rh
- Aspirated Thermocouple
- Probe Corrected for Radiation and Conduction
Figure 14. Probe-measured temperature profile across IFRF combustor flame No. 6 – $\phi = 1.2$. 

- Pt/Pt - 13 percent Rh Aspirated Thermocouple Probe Corrected for Radiation and Conduction
Figure 15. Modified FT-12 burner can assembly.
Figure 16. Normalized probe-measured NO and NOx concentration profiles across optical axis for FT-12 combustor – idle.
Figure 17. Normalized probe-measured NO and NO\textsubscript{x} concentration profiles across optical axis for FT-12 combustor — cruise.
Figure 18. Normalized probe-measured NO and NO\(_x\), concentration profiles across optical axis for FT-12 combustor.
Figure 19. Probe-measured temperature profile across optical axis for FT-12 combustor - idle.
Figure 20. Probe-measured temperature profile across optical axis for downstream of FT-12 combustor – cruise.
Figure 21. Probe-measured temperature profile across optical axis for downstream of FT-12 combustor — maximum continuous.
Figure 22. Atmospheric pressure combustion facility.
1. Iteration proceeds until $\varepsilon \rightarrow 0$.

2. For cylindrically symmetric absorbing medium, procedure is repeated for each successive measurement path.

Figure 23. Illustration of resonance absorption technique for nitric oxide measurements.
Figure 24. Schematic of AEDC absorption system used at UTRC.
Figure 25. Typical NO (0,0) γ-band absorption spectra from flat-flame burner.
Figure 26. Typical NO (0,0) $\gamma$-band absorption spectra from IFRF combustor.
Figure 27. Typical NO (0,0) $\gamma$-band absorption spectra from FT-12 combustor.
Figure 28. Calibration curves of NO using second bandhead of the (0,0) \( \gamma \)-band for the flat-flame burner, IFRF combustor and FT-12 combustor.
b. IFRF combustor

Figure 28. Continued.
c. FT-12 combustor
Figure 28. Concluded.
Figure 29. Ratio of optically and probe-measured NO concentration to seed + production versus equivalence ratio (\(\phi\)) for flat-flame burner.
Figure 30. Ratio of optically and probe-measured NO concentration to seed + production versus equivalence ratio ($\phi$) for IFRF combustor.
Figure 31. Ratio of optically and probe-measured NO concentration to seed + production versus equivalence ratio ($\phi$) for FT-12 combustor.
Altitude = 11 km
Mach Number = 0.95
$P_{\text{cell}} = 23$ kPa
$P_l = 48.5$ kPa
$T_l = 266^\circ$K

Figure 32. Revised NO concentration profile for F101-GE-100 engine.
Table 1. Results of Optically and Probe-Measured NO Concentration in Flat-Flame Burner.

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Table 2. Results of Optically and Probe-Measured NO Concentration in IFRF Combustor Exhaust.

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<td>°K</td>
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Table 3. Results of Optically and Probe-Measured NO Concentration in FT-12 Combustor Exhaust.

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