



Project Summary

Fundamental Combustion Research Applied to Pollution Formation—Volume III. Support Studies: Measurement Studies

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This is the third volume in a series documenting research activities conducted under the EPA's Fundamental Combustion Research (FCR) program, applied to pollution formation. The FCR program had three major objectives:

- To generate an understanding of combustion behavior necessary to aid in developing control strategies to minimize NO_x emissions from stationary sources.
- To develop engineering models which would allow effective utilization of a large body of fundamental information in the development of new NO_x control techniques.
- To identify critical information necessary for low-NO_x combustor development and to generate it in a time frame which was consistent with the needs of EPA's technology development programs.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

This report documents findings from a limited number of studies to evaluate measurement techniques. FCR program efforts to evaluate and develop measurement techniques were conducted as part

of a support function to the overall FCR program. An overview of the entire FCR program content and the objective of the program's various components are presented in Volume I. Volume I also describes FCR program efforts to quantify the gas-phase chemistry controlling NO_x formation and destruction during combustion. Volume II is a three-part report describing studies related to various aspects of the physics and chemistry of two-phase systems: Volume IIa addresses flame combustion processes, Volume IIb addresses devolatilization and volatile reactions, and Volume IIc describes studies of heterogeneous NO reduction processes. Volume IV documents FCR program efforts to develop engineering analysis computer models.

The prime contractor and EPA's project officer were responsible for program planning, management, and synthesis of the overall combined inhouse and sub-contract program. Approximately 70% of the program effort involved subcontracts to a variety of organizations throughout the world, ensuring that the FCR program had the benefit of the best scientific talent available.

A substantial fraction of the experimental studies reported in Volumes I, II, and III were conducted through subcontracts or were joint efforts involving both EER and a subcontractor. Most of the modelling, however, was performed by EER directly. Volume III gives results from three individual research projects. The first study reported, performed directly by EER, evaluated potential errors involved in the chemiluminescent measurement

of NO in combustion products. The second study, performed through a subcontract to the University of Utah, included an assessment of the procedures required to measure nitrogenous intermediates involved in staged combustion. The final portion of Volume III documents results from a joint study conducted by EER and Spectron Development Laboratories to assess optical droplet sizing techniques which might be applied to studies of pollutant formation in liquid fuel spray flames. Each study is presented as a separate report with individual tables of contents, lists of figures, conclusions, and references. The remainder of this Project Summary presents brief descriptions of the individual components comprising Volume III.

Chemiluminescent Measurement of NO in Combustion Products

The measurement of nitric oxide (NO) concentrations in combustion products by chemiluminescence has several advantages over alternative methods. As a result, the chemiluminescent NO analyzer (CLA) has become a standard instrument for most laboratory and field emissions tests. CLAs were used by EER and all FCR program subcontractors for NO_x measurements reported in this report series. During the FCR program, several papers appeared in the literature questioning the accuracy of CLAs when calibrated using NO in an N₂ background for the span gas. (The primary concern

was that background gas composition affected the NO concentration measurement.) Molecular nitrogen represents the dominant species in traditional combustion exhaust products, but there are also substantial concentrations of other species (e.g., water vapor and CO₂). One paper indicated that the common practice of neglecting background gas composition variation could introduce errors as large as 28% in indicated NO concentration. This was an issue of considerable concern to the FCR program and to the EPA. Accordingly, a research project was initiated with three objectives:

- Assess the accuracy of commercial CLAs measuring NO in combustion products following the calibration and operating procedures recommended by the instrument manufacturers.
- Examine methods of correcting CLA-indicated NO concentrations for the effects of background gas composition variations.
- Examine methods to improve calibration procedures.

Figure 1 is a simplified schematic of a CLA NO analyzer. A flow of ozone is mixed with the sample gas in the reaction chamber. The ozone and NO in the sample gas (or span gas) rapidly react to form nitrogen dioxide in either an excited state (NO₂^{*}) or a ground level state (NO₂). The yield of NO₂^{*} is about 10% at ambient temperatures. The excited molecules can

decay to ground state giving off light of a characteristic frequency (chemiluminescence) or can collide with any third body (M) and decay to ground state without chemiluminescence (quenching). The relative importance of the chemiluminescent and quenching reactions depends upon the temperature, and the amount and type of molecules available for quenching (i.e., the background gas composition). The intensity of chemiluminescence, measured with a photomultiplier tube (PMT), is directly proportional to NO concentration. The relation between PMT output and NO concentration is determined by calibrating the instrument using a known concentration of NO in a background gas to adjust the amplifier gain. A span gas which is NO free is used to adjust zero offset and to account for PMT dark current effects.

The previously noted literature reports indicating substantial CLA NO measurement error were primarily concerned with the third body quenching efficiency of major combustion product gases (e.g., H₂O and CO₂) relative to that of N₂. These reports presented experimental evidence showing the strong impact of background gas composition on the quenching process. Background gas composition can also influence other important features of CLA operation. A potential influence of background gas composition is its impact on sample gas flow rate to the reaction chamber. It is important to recognize that the output from the CLA's

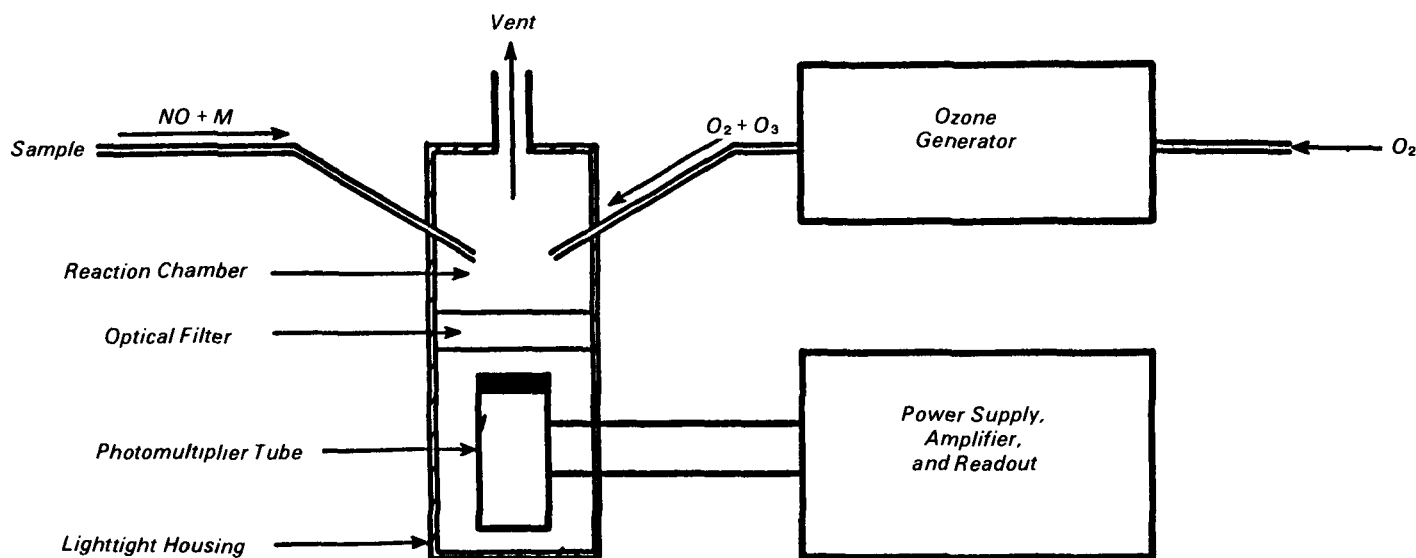


Figure 1. Chemiluminescent measurement of NO.

PMT is actually proportional to the number of NO molecules entering the reaction chamber, not simply the NO concentration. For that reason, any process that impacts the flow rate of sample gas to the reaction chamber will also affect the NO concentration indicated by the CLA. Commercial CLAs typically control flow rates by passing the sample gas (and span gas) through a capillary and regulating the capillary pressure drop. Note, however, that for a constant pressure drop, the flowrate through a capillary is inversely proportional to the gas viscosity. Variations in sample gas composition which alter the average viscosity will result in variation in sample flowrate and the indicated NO concentration. This potential source of CLA measurement bias was not considered in the above noted reports dealing with the quenching process. Fortunately, for the major non-N₂ constituents of typical combustion products, biases due to quenching and viscosity effects are in opposite directions.

To accomplish the program objectives, two commercially available CLAs were zeroed and spanned with N₂ and NO in N₂, respectively, and then used to measure known concentrations of NO in a variety of background gases. The gas mixtures were prepared by blending high purity gases and mixtures of NO in carrier gases in a precision flow metering system. The gas mixtures simulated combustion products from a wide range of fuel compositions and combustor operating conditions. The NO concentrations indicated by the CLAs were then compared with the actual NO concentrations to determine the effects of background gas composition. Two commercial CLAs selected for evaluation: a Beckman Model 951 and a Thermal Electron Corporation (TECO) Model 10A. The major distinction between the instruments is that the Beckman is designed to operate with the reaction chamber at atmospheric pressure, while the TECO utilizes a subatmospheric pressure (nominally 9 torr¹) reaction chamber. These pressure differences were expected to highlight the influence of the quenching process on NO measurement.

The experimental program consisted of three series of tests. The Series 1 sample gas consisted of NO in a background of

N₂ and varying percentages of another gas. Figure 2 illustrates the response of both instruments to varying (but large) concentrations of O₂, CO₂, CO, and CH₄ in the background gas. In typical combustion system exhausts, the O₂ concentration will be less than 20% (assuming combustion in air), the CO and CH₄ concentrations should be in the ppm range, and the CO₂ concentration will be on the order of 10%. As shown, the impact of these sample gases on CLA operation is to decrease the indicated NO concentration. The atmospheric pressure reaction cell of the Beckman instrument showed a slightly stronger bias.

Series 2 simulated background gases that would be produced in actual combustion systems (as opposed to the binary mixtures examined in Series 1). Background gas mixtures were prepared simulating the products of complete combustion for a range of fuels at variable excess air levels. The fuels considered were methane and pure carbon, representing the extremes in fuel-carbon/hydrogen ratio. The fuel/air ratio simulated ranged from stoichiometric all the way to an infinite excess air level. Figures 3A and 3B show the response of the TECO and Beckman instruments to sample gases containing 200 ppm NO. Figure 3C shows the response of both instruments to different NO levels as a function of theoretical air but holding

the fuel type constant. These figures illustrate that the anticipated error from the TECO instrument will be less than 5% for all conditions analyzed. For the Beckman instrument, the influence of other background gases was found to be much stronger, with errors as large as 11% indicated in the 100% theoretical air range.

The usual procedure in commercial CLA operation is to draw the sample gas through an ice bath (or through a dryer) to remove water from the sample and to reduce the sample dewpoint to below room temperature. As part of Series 2, experiments were conducted which varied the sample dewpoint in the range of 275-294 K. The impact of sample dewpoint on indicated NO level was found to be small for the TECO instrument (1-2%), but substantial for the Beckman instrument (up to 6%).

Series 3 evaluated the impact of using CLAs spanned on NO in N₂ to measure the NO concentration from combustion experiments using artificial oxidizers. As part of the FCR program and EPA's inhouse research program, experiments were conducted in which argon or an argon/CO₂ mixture replaced molecular nitrogen in the combustion air. Such artificial oxidizer tests were used to evaluate the contribution of fuel bound nitrogen to exhaust NO. This particular combustion situation was expected to

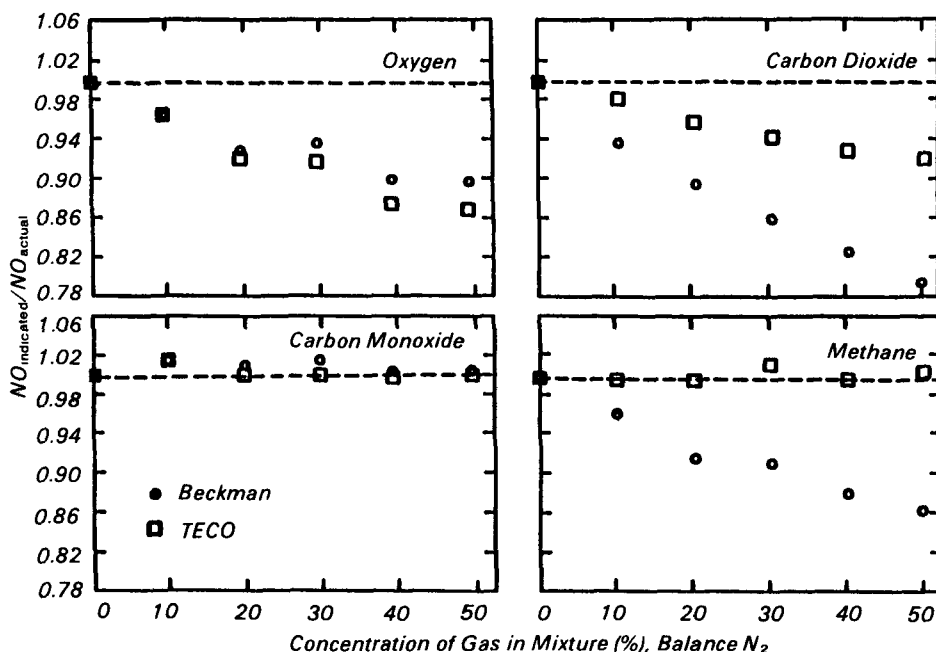


Figure 2. Binary background gases on impact of chemiluminescent NO measurement.

¹To convert to the metric system 1 torr = 133 Pa

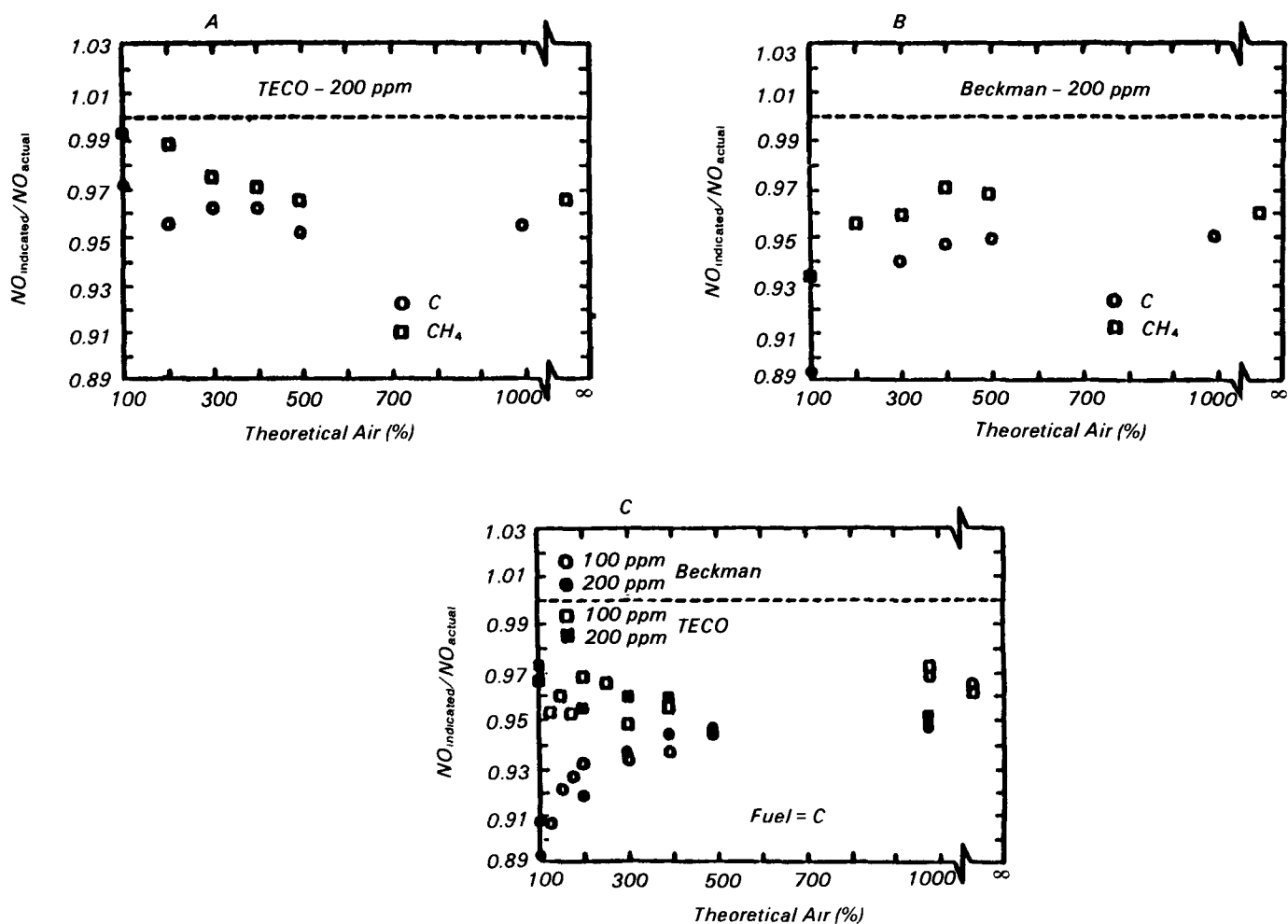


Figure 3. Impact of fuel type and excess air level on NO measurement using chemiluminescent analysis.

result in large instrument errors since the anticipated bias from argon quenching effects are in the same direction as the bias from variation in sample flow to the reaction cell. Results from Series 3 are shown in Figure 4 and clearly demonstrate the anticipated result. For the TECO instrument, the indicated concentration was low by 14-18%. For the Beckman instrument, the measurement error is a relatively strong function of excess air level, but errors as large as 20% are observed. Based on these examinations of CLA bias for argon-substituted combustion air, it is suggested that the CLA response be carefully calibrated and experimental results corrected for the instrument bias. Alternately, special calibration gases with argon/CO₂ mixtures as the background gas should be used.

Measurement of Nitrogenous Intermediates in a Staged-Combustion System

A small FCR program subcontract was issued to the University of Utah to assess various techniques being used to measure nitrogenous intermediates from staged combustion processes. The primary focus of the study was evaluation of specific ion electrodes for the measurement of hydrogen cyanide (HCN) and ammonia (NH₃) concentrations generated in staged combustion flames. Three important introductory notes are in order. First, HCN and NH₃ are formed as intermediate species in the process of converting fuel bound nitrogen into either NO or N₂. These intermediates are not expected as constituents in the exhaust gas of traditional or staged

combustion processes. The second introductory note is that this study was not intended as an exhaustive evaluation of nitrogenous intermediate measurement techniques. Within the FCR program and the combustion research community in general, specific ion electrodes are widely used to determine the concentration of HCN and NH₃. There was, however, wide variation in the details of how samples were collected and the procedures used for sample analysis. The study conducted at the University of Utah was focused on evaluation of the various procedures being employed by other FCR research organizations. Finally, it should be noted that emphasis is placed on extracting samples from within the flame zone of a furnace fired with coal or residual fuel oil. This is an extremely hostile environment which impacts how

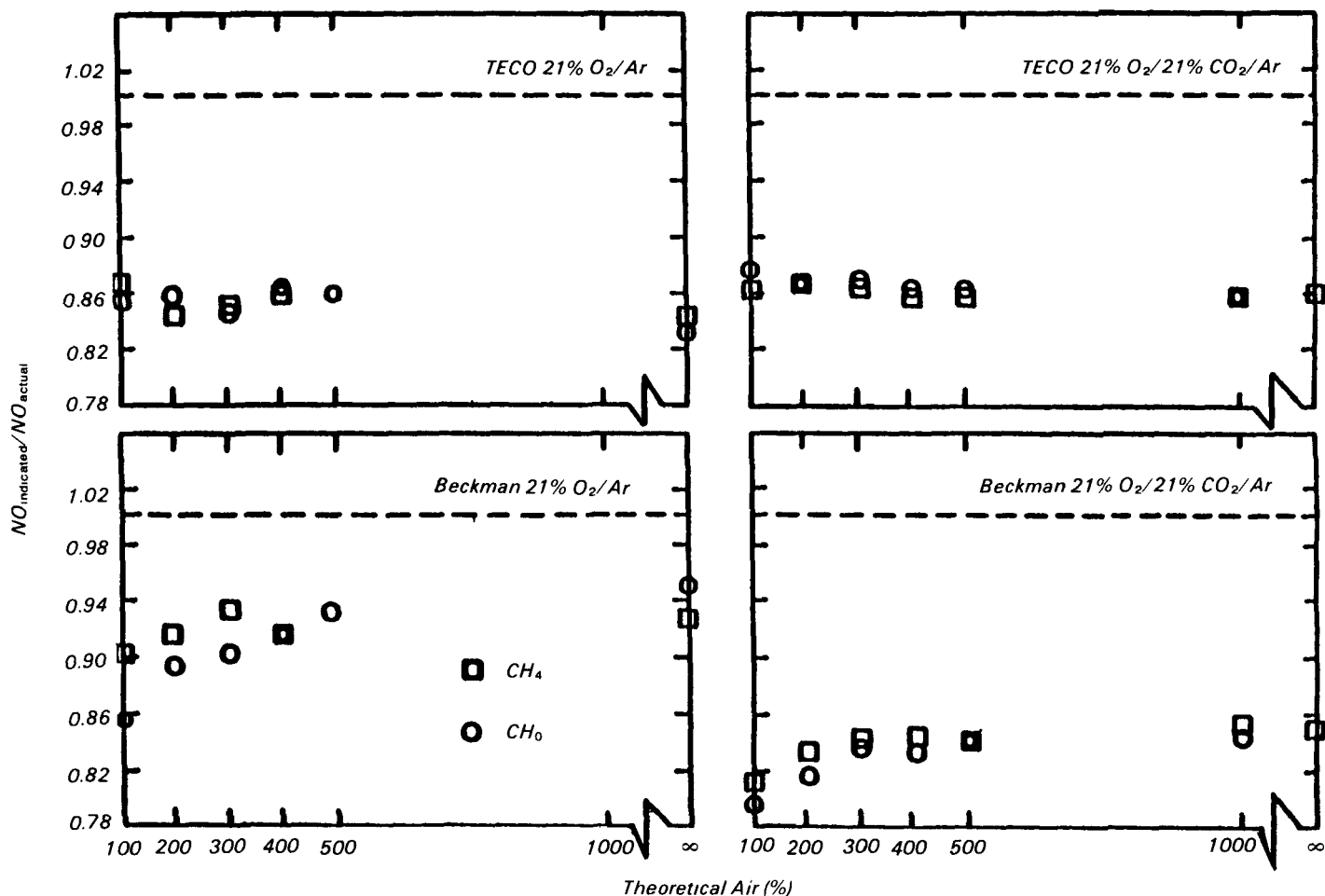


Figure 4. Influence of O_2/Ar and $O_2/CO_2/Ar$ artificial oxidizers on measurement of NO from combustion tests using chemiluminescent analyzers.

the sampling probes must be designed and operated if the probe is to survive mechanically.

The study was performed through separate analysis of NH_3 and HCN measurement procedures and included evaluation of sample collection, sample preparation, and sample analysis. Specific ion electrode for NH_3 measurement was evaluated first. The initial portion of the study centered on procedures for using the specific ion electrode itself. Effects of sample solution temperature, pH effects, and ionic strength effects on NH_3 concentration measurement were all evaluated. In general, results from this evaluation confirmed the electrode manufacturer's operating instructions and suggestions.

To collect a sample for analysis it is necessary to drive the NH_3 in the sample gas into solution. Figure 5 illustrates the probe and sampling system found to be most appropriate for that purpose. The

top portion of Figure 5 is a schematic of the spray probe which was used for furnace sampling at the University of Utah. The probe body is water-cooled and of stainless steel to withstand the high temperature environments from which sample gases must be extracted. A small tube is on the centerline of the probe. Small holes at the end of this tube admit a spray of water or other collecting solution into the sample gas flow. This spray serves to both cool the sample gas and drive the NH_3 into solution. The combined sample gas and liquid from the spray are directed to a series of impingers at the probe outlet. Sampling system components downstream of the impingers measure the sample gas flow rate. Extensive evaluations were conducted to evaluate the influence of spray composition, type of bubblers or impingers, type and quantity of contacting solution in the impingers, and effects of sample flow rate and NH_3 concentration in the sample

gas. These evaluations indicated that distilled deionized (DD) water for the spray collection efficiency of 97% was achieved (sampling 5 L/min of 550 ppm NH_3 , balance N_2) with the spray probe itself. Adding fritted bubblers on the probe outlet increased the collection efficiency to 98%. Changing the spray and bubbler solution from DD water to 0.1 N H_2SO_4 increased the collection efficiency to 99%.

The final portion of the ammonia probe study included assessment of potential interference effects from other species in the sample gas. Strong interferences were found for two gases: when the sample gas contained dimethylamine, a strong positive interference was observed, indicating that the electrode is not totally specific to NH_3 but also senses NH species; and a strong negative interference was found for SO_2 . Further investigation indicated that a substantial

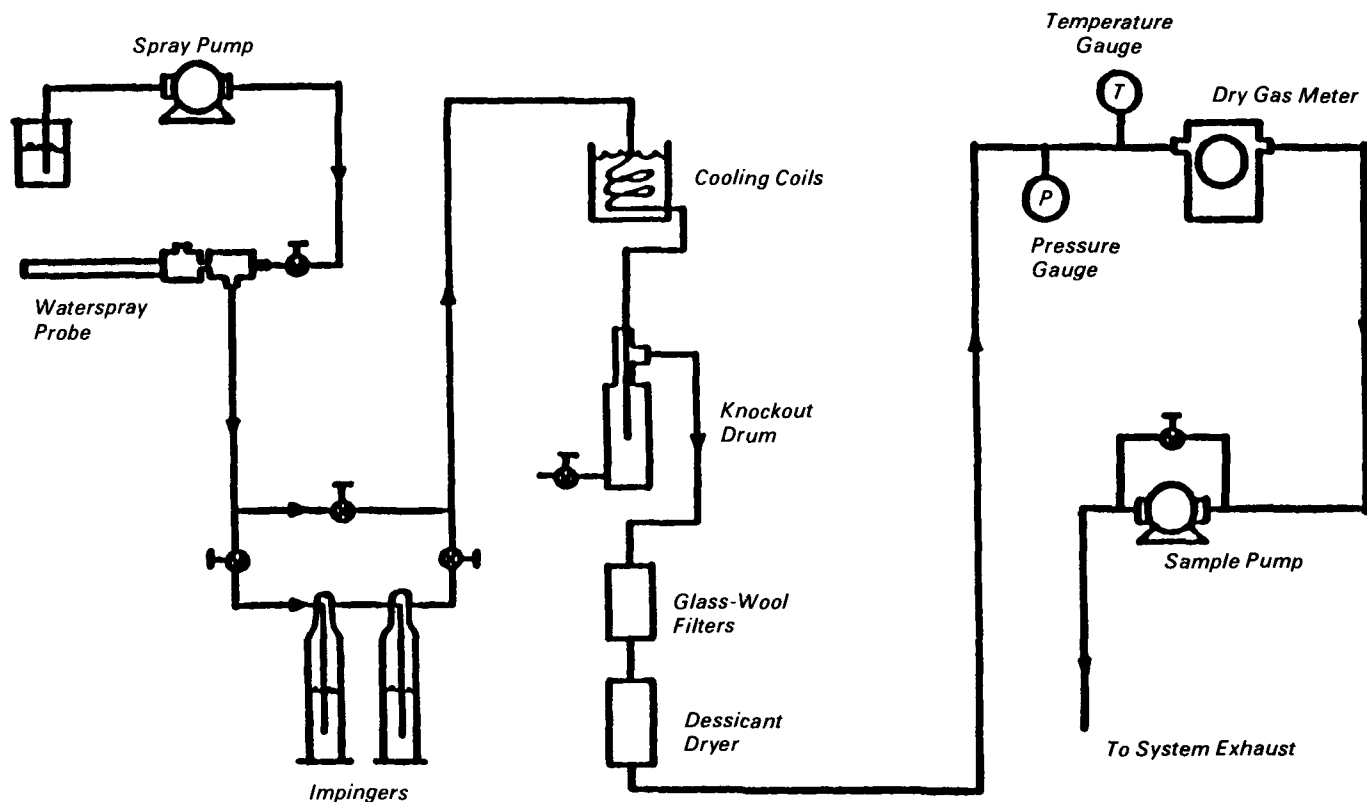
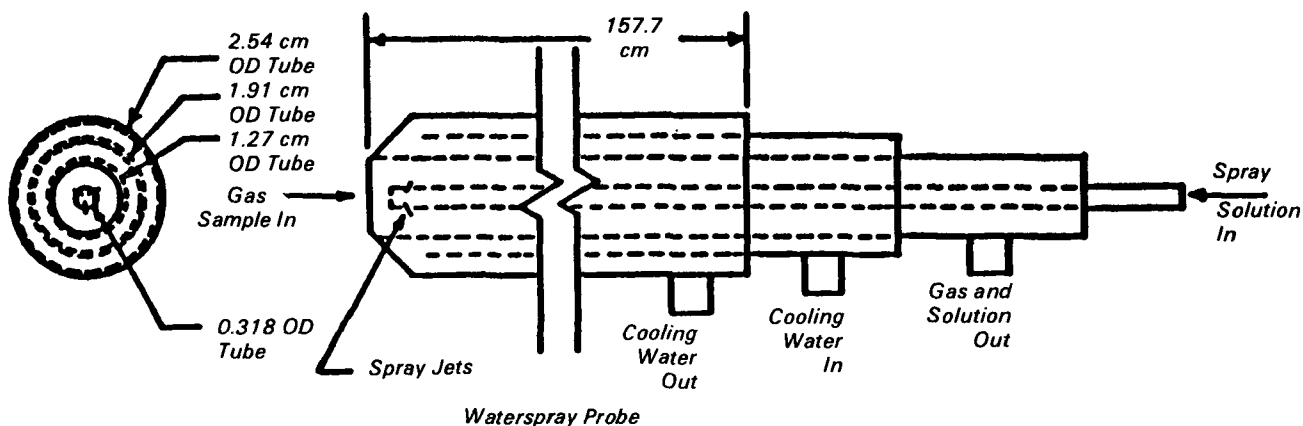


Figure 5. Waterspray probe and sampling system.

fraction (not quantified) of the SO_2 interference was the result of gas-phase reactions between NH_3 and SO_2 prior to the sample gas reaching the sampling probe. The need for further evaluation of this interference is indicated.

Evaluation of the HCN measurement system proceeded similarly to the eval-

uation of the NH_3 probe. The specific ion electrode evaluation included assessments of the impacts of solution temperature, pH effects, and ionic strength impacts on the electrode response. As with the NH_3 electrode, the cyanide electrode performs in much the fashion indicated by the instrument manufac-

turer. However, an observed hysteresis effect suggested that the cyanide electrode be conditioned with a solution of low cyanide concentration in comparison with the solution on which measurements are to be made.

The optimal sample collection system for HCN was found to be the same a

that for the NH_3 system shown in Figure 5. A variety of spray solutions and contacting solutions in the impingers were investigated. Using DD water, 0.1 N H_2SO_4 , and 1.0 M NaOH , all resulted in HCN collection efficiencies of only about 85%. Evaluations of interfering gas species in the sample flow found that the only major interference came from S^- . Addition of Bi^{+3} to the impingers was found effective for removal of both the S^- ion and its interfering effect.

A final portion of the University of Utah study reports on experiments to measure nitrogenous intermediates in a staged combustion system. Experiments were conducted in a refractory tunnel furnace and burned natural gas doped with surrogate fuel nitrogen compounds in a staged combustion configuration.

Spray Characterization

An FCR experimental research project was jointly conducted by EER and Spector Development Laboratories (SDL) to evaluate three laser-based techniques for measuring characteristics of sprays. A number of optical techniques have been developed or proposed which promise information on spray parameters such as the spatial distribution of drop size distribution and the velocity of

various drop size classes. The three techniques evaluated in this FCR project included processes based on interferometry, holography, and laser diffraction.

Interferometry, a point measurement technique, can simultaneously determine the diameter and velocity of a droplet passing through the point sampling volume. Droplet diameter and velocity distribution information can be obtained at a given probing location, while spatial distribution of size distribution and velocity is obtained by sequentially examining multiple locations in the spray. Holography provides an instantaneous, three-dimensional picture of the droplet field and was included in the evaluation as a cross-check for the interferometry and diffraction techniques. The diffraction technique examined provided a line-of-sight measurement of drop size distribution and did not provide information on droplet velocity. It was included in the evaluation because the technique rapidly provides processed data and because it had been used for spray nozzle characterization in a previous EPA study conducted at the International Flame Research Foundation (IFRF) in IJmuiden, Holland.

To evaluate the measurement techniques, a special spray chamber was

constructed from a 0.61 m diameter Plexiglas tube to simulate the geometry of EPA's firetube package boiler simulator. Commercial spray nozzles could be located on the chamber centerline, while an adjustable quantity of air was provided co-axial to the nozzle. Initial testing was restricted to a small twin-fluid atomizer (Sonicore model 052 H) which had been used in several combustion evaluation studies. This Sonicore nozzle had also been evaluated as part of the previously noted IFRF spray characterization study.

The laser interferometry study utilized optical hardware and signal processing equipment provided by SDL (see Figure 6). Light from a helium-neon (HeNe) laser was split into two beams by a diffraction grating and then crossed within the spray chamber. At the beam intersection, an interference fringe pattern is established. When a droplet passes through this probe volume, light is scattered and collected on a photomultiplier tube. Analysis of the resultant electrical signal provides information on the droplet diameter and velocity. Data from multiple droplets passing through the probe volume are stored on a computer disk and analyzed to define histograms of droplet size and velocity.

The laser holography system, also provided by SDL, consisted of an HeNe

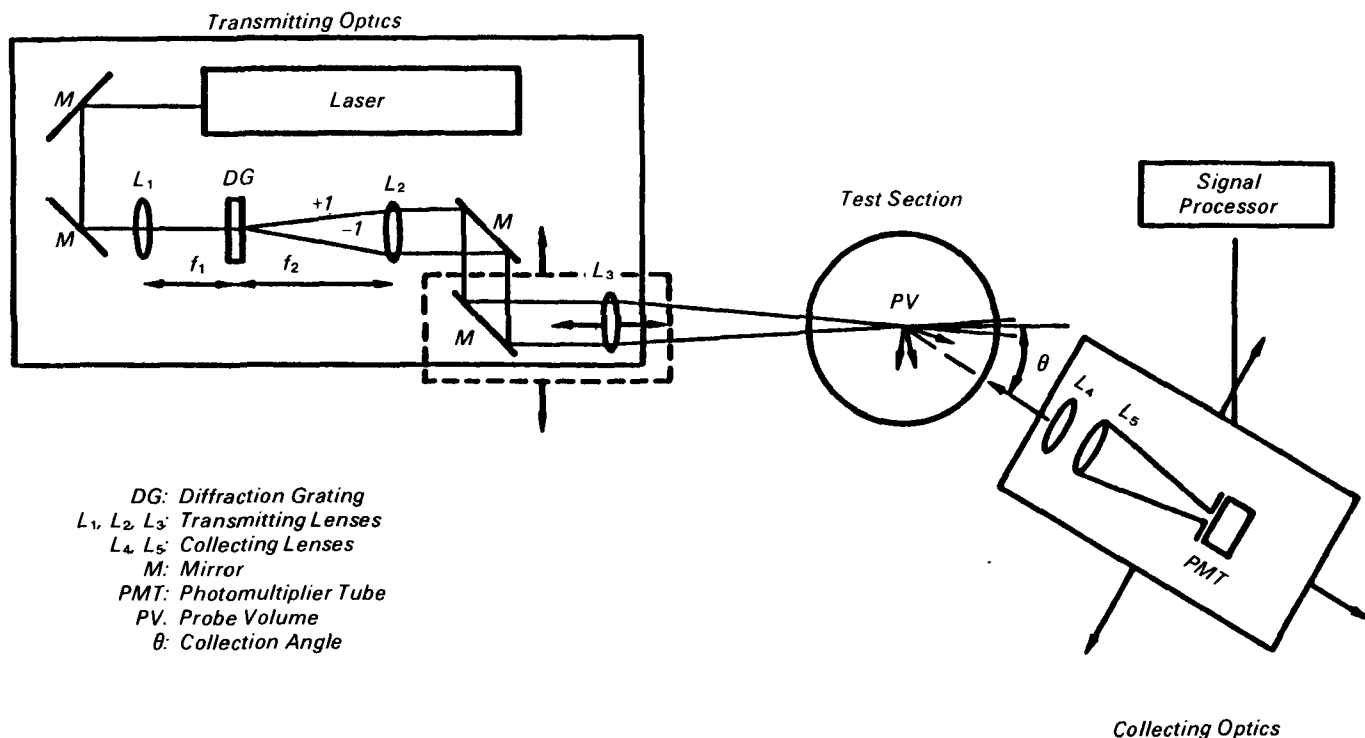


Figure 6. Laser interferometry system.

laser for alignment and a ruby laser to take the hologram. The ruby laser beam was split into information and reference beams. Both beams were expanded, spatially filtered, and collimated. The information beam went through the fuel spray, while the reference beam bypassed the test section. The two beams were then mixed on a hologplate. The optical configuration employed produced a probe volume on the order of 10 cm^3 . A shutter in front of the hologplate holder allowed light to enter only during recording and minimized the influence of extraneous light sources.

The laser diffraction system employed was the Malvern Model 1800 purchased by EPA for the previously mentioned IFRF study. The basic measurement system consists of an HeNe laser whose beam is expanded to 6.0 mm diameter and passed through the spray flow field. Light from the beam is diffracted by droplets in the spray. The angle of diffraction depends on the droplet diameter, increasing with decreasing droplet size. As illustrated in Figure 7, the diffracted light is collected by a Fourier transform lens and focused on a 30-ring detector. The distribution of light energy across the 30 rings is read by a minicomputer and fit to a Roslin-Rammler distribution. The sweep time of the detector is approximately 13 msec. A representative droplet size distribution is obtained by averaging the results from about 100 to 200 sweeps.

Figure 8 illustrates typical results from the evaluation in a plot of spray weight density distribution versus droplet diameter for the three measurement techniques. These data were all collected at the same axial location in the spray with the same nozzle operating conditions. The diffraction and holography techniques are in reasonable agreement; the major source of deviation is attributed to failure of the holography system to detect droplets smaller than about 15-20 μm in diameter. Both the diffraction and holography techniques give results in marked contrast to the interferometric technique. This discrepancy is attributed to the limited dynamic range of the interferometric technique. The technique is capable of measuring droplets within only a 1 decade variation range in diameter. As noted in the figure, the diffraction technique detected droplets ranging from <10 to $>200 \mu\text{m}$ diameter. The interferometer tests were conducted to measure droplets in the range of approximately 10-100 μm . Centering of the dynamic range is adjustable, but

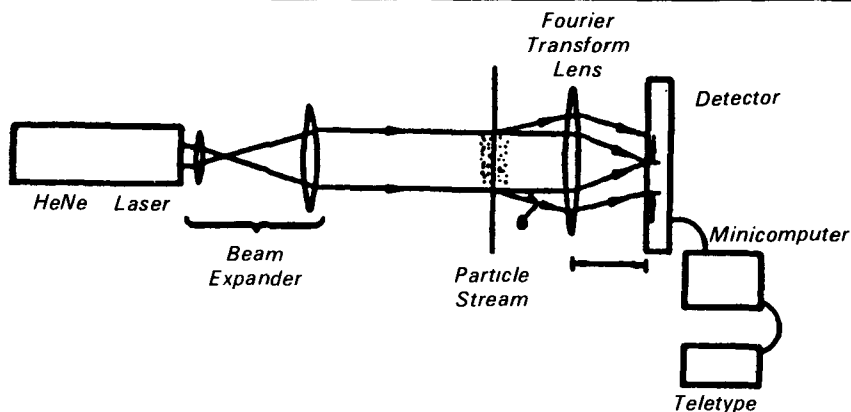


Figure 7. Laser diffraction diagnostic technique.

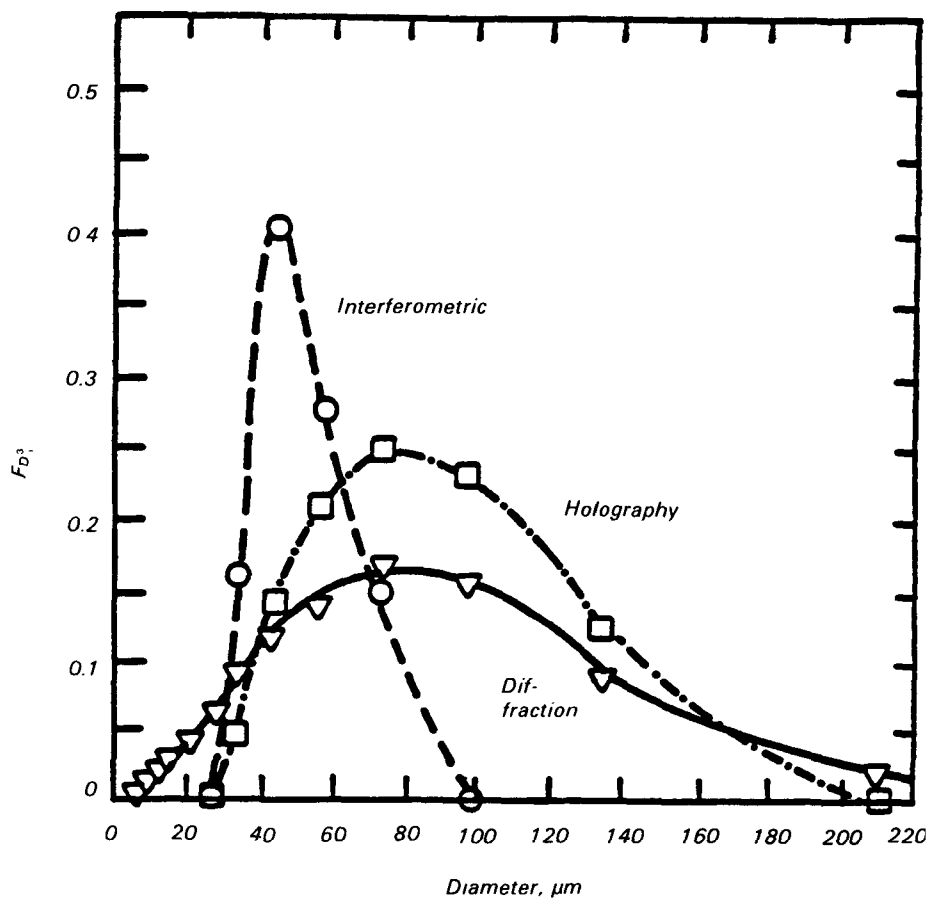


Figure 8. Interferometric, diffraction, and holography data—weight density distribution for Sonicore spray nozzle.

biasing resulting from the limited dynamic range appears to be a major drawback to the technique. It is important to note that SDL felt that many of the apparent shortcomings of the interferometer technique were a matter of data interpretation. An appendix in the report documents the evaluation position taken by SDL.

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The complete report, entitled "Fundamental Combustion Research Applied to Pollution Formation: Volume III. Support Studies: Measurement Studies," (Order No. PB 88-168 968/AS; Cost: \$38.95, subject to change) will be available only from:

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