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WRDC-TR-90-2079
Volume 1

ADVANCED THERMALLY STABLE JET FUELS DEVELOPMENT PROGRAM ANNUAL REPORT

VOL 1 - MODEL AND EXPERIMENT SYSTEM DEVELOPMENT

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September 1990

INTERIM REPORT FOR THE PERIOD JUNE 1989 - JUNE 1990

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REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No 0704-0188*
1a REPORT SECURITY CLASSIFICATION Unclassified	1b RESTRICTIVE MARKINGS None
2a SECURITY CLASSIFICATION AUTHORITY N/A	3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; Distribution is unlimited
2b DECLASSIFICATION/DOWNGRADING SCHEDULE N/A	
4 PERFORMING ORGANIZATION REPORT NUMBER(S) N/A	5. MONITORING ORGANIZATION REPORT NUMBER(S) WRDC-TR-90-2079, Vol 1.

6a NAME OF PERFORMING ORGANIZATION Sandia National Laboratories	6b OFFICE SYMBOL *(If applicable)*	7a. NAME OF MONITORING ORGANIZATION Aero Propulsion and Power Lab WRDC AFSC
6c. ADDRESS *(City, State, and ZIP Code)* Albuquerque, NM 87185		7b. ADDRESS *(City, State, and ZIP Code)* WRDC/POSF Wright-Patterson Air Force Base, OH 45433-6563
8a NAME OF FUNDING/SPONSORING ORGANIZATION N/A	8b. OFFICE SYMBOL *(If applicable)* N/A	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER FY1455-89-N0635

8c. ADDRESS *(City, State, and ZIP Code)*
N/A

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
62203F	3048	05	81

11 TITLE *(Include Security Classification)*
Advanced Thermally Stable Jet Fuels Development Program Annual Report
Vol 1 - Model and Experiment System Development

12 PERSONAL AUTHOR(S)
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13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT *(Year, Month, Day)*	15. PAGE COUNT
Interim	FROM 6/89 TO 6/90	September 1990	80

16. SUPPLEMENTARY NOTATION

17. COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
Jet Fuels, Thermal Stability, Coking,
Thermal Degradation, Fouling, CFD Models,
High Temperature Fuels, Laser Diagnostics

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

A program entitled "Thermally Stable Jet Fuels Development" was initiated in FY89 by the U.S. Air Force, Aero Propulsion and Power Laboratory, working jointly with the Department of Energy, Pittsburgh Energy Technology Center. Aviation turbine fuel thermal stability is of concern because of the potential operational problems arising from the degradation of fuels when used to cool aircraft components. Within this program, investigations are proceeding to develop candidate advanced thermally stable fuels, kinetic models of fuel degradation and to measure parameters for computational fluid dynamic models to predict the degradation of fuel under various conditions. This report summarized efforts in the first year of the program to identify specific processes and parameters involved in fuel thermal degradation and to develop diagnostic instrumentation and experiment apparatus that can be used to obtain data for model development.

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a NAME OF RESPONSIBLE INDIVIDUAL William E. Harrison III	22b TELEPHONE *(Include Area Code)* 513-255-6601	22c. OFFICE SYMBOL WRDC/POSF

DD Form 1473, JUN 86 *Previous editions are obsolete.*

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FOREWORD

In May 1989, the Fuels Branch of the Aero Propulsion Laboratory at Wright-Patterson Air Force Base, Ohio, commenced an investigation to develop advanced, thermally stable jet fuels as well as physical and computer models that could simulate the thermal degradation of those fuels under operational conditions. Funding was provided to the Department of Energy (DOE) Pittsburgh Energy Technology Center (PETC) to administer this effort. This report, Volume 1 of 3 volumes, details the efforts of Sandia National Laboratories (SNL), who, as a contractor to DOE (DOE Contract Number DE-AC04-76DP00789), investigated diagnostic techniques that could be used to obtain data on liquid- and solid-phase characteristics necessary for model development and development an experiment system for measuring those characteristics. Mr. William E. Harrison III was the Air Force Program Manager, Dr. Nand Narain, Dr. Richard Hickey, and Mr. Swenam Lee were the DOE/PETC Program Managers, and Dr. Howard Stephens was the SNL Program Manager.

TABLE OF CONTENTS

FIGURES

FIGURES

TABLES

Acknowledgements

This Project was jointly supported by the U.S. Department of Energy, Pittsburgh Energy Technology Center (PETC) and the WRDC/Aero Propulsion and Power Laboratory, Wright-Patterson AFB. This work was supported by the U.S. Department of Energy at Sandia National Laboratories under contract DE-AC04-76DP00789. The authors wish to express their appreciation to Messrs. N. K. Narain, R. Hickey, S. Lee, and M. Baird (PETC) and Mr. W. E. Harrison III (WRDC/Aero Propulsion and Power Laboratory) for their support of this effort. The authors would like to acknowledge Messrs. W. M. Roquemore, J. A. Pearce, and J. Moler (WRDC/Aero Propulsion and Power Laboratory) for their technical input and guidance. The authors would also like to acknowledge R. J. Kottenstette, H. P. Stephens, D. M. Haaland, A. S. Geller, W. M. Trott, S. J. Martin, A. J. Lammie, B. J. Lammie, D. S. Blair, J. J. Stephens, Jr., G. C. Nelson, K. L. Higgins, F. V. Stohl, and R. C. Givler (Sandia National Laboratories) for their technical support.

I. INTRODUCTION

Thermal stability of aviation fuels is of concern because of the potential operational problems arising from fuel degradation under thermal stress conditions. Hydrocarbon fuels in contact with heated metallic surfaces form insoluble, carbonaceous deposits that can foul nozzles, manifolds, filters, injectors, and heat exchangers. Temperatures in current aircraft reach approximately 163°C (325°F); temperatures in future aircraft, with expected speeds above Mach 4, are expected to reach over 627°C (1160°F). The methods of dissipating the large heat loads will be one of the key factors in determining the capabilities of future aircraft. The use of heat exchangers in which the fuel is used as the primary or secondary coolant appears to be an effective way of dissipating heat. While currently used jet fuels are thermally stable within present aircraft operational limits, the anticipated increases in the thermal loading applied to fuel systems of high-performance aircraft have prompted the development of advanced, thermally stable aviation fuels and methods to predict the stability of these fuels under varying operating conditions.

Although jet fuels can be used as a coolant, there are temperature operating limits for all hydrocarbon fuels at which the fuels break down to form solids and gums that clog filters, cause sticking in fuel control valves, and foul heat exchangers and fuel nozzles. Currently used jet fuels begin to degrade at temperatures above approximately 163°C (325°F). The degradation of jet fuels and subsequent formation of solid deposits depend on fuel composition, fluid dynamics, and heat transfer and mass transport characteristics. Hydrocarbon fuel thermal stability has been studied for many years by numerous investigators employing a variety of test methods. Few investigations, however, have attempted to develop quantitative models of the fluid dynamics, heat transfer, mass transport, and chemical kinetic processes that occur during thermal stressing of fuels in aviation fuel systems. Mathematical models of the coupled physical processes occurring in a fuel system are required to predict the thermal stability of different fuel mixtures under varying operating conditions.

A long-term effort to develop thermally stable fuels for aircraft was initiated in FY89 by the U.S. Air Force, working jointly with the Department of Energy, Pittsburgh Energy Technology Center. Sandia National Laboratories, Albuquerque, is the lead laboratory within the Advanced Thermally Stable Jet Fuels Development Program in conducting efforts to (1) develop candidate advanced, thermally stable fuels and kinetic models for their thermal degradation and (2) develop the capability to predict the fuel thermal stability (i.e., the amounts, characteristics, and locations of solid deposits) under given operating conditions. Investigations to support these objectives include studies of model compounds and mixtures representative of petroleum- and coal-derived fuels to correlate thermal stability with composition and determine reaction mechanisms; lubricity investigations on candidate high-temperature additives for these jet fuels;

This work was supported by the U.S. Department of Energy at Sandia National Laboratories under contract DE-AC04-76DP00789.

development of mathematical models of the physical and chemical processes occurring in an aviation fuel system; and the development of instrumentation and apparatus that can be used to obtain data necessary for model development and also be used as diagnostic tools to evaluate candidate fuels. Investigations to develop advanced, thermally stable jet fuels are being performed by Pennsylvania State University; the activities performed in the first year of the program are documented in a separate report, "Advanced Thermally Stable Jet Fuels Development Program Annual Report, Volume II. Compositional Factors Affecting Thermal Degradation of Jet Fuels" (Eser et al., 1990). Those studies involved tests of the thermal stability of model compounds and of jet fuels to obtain data relating structural characteristics of fuel components to their thermal stability. Studies to evaluate high-temperature lubricity additives are being performed at Southwest Research Institute and are documented in "Advanced Thermally Stable Jet Fuels Development Program Annual Report, Volume III. Lubricity Studies" (Cuellar Jr. et al., 1990). The lubricity studies have included acquisition of candidate high-temperature lubricity additives, modification of an existing lubricity-testing apparatus to allow high-temperature operation, and evaluations of the lubricity capabilities of the candidate additives. Activities related to the development of predictive models and development of experiment apparatus for thermal stability data acquisition are described in this report. During this first year of the program, efforts have focused on identification of the processes and parameters that are important to fuel degradation and solids deposition in an aviation fuel system, the development of a thermal stress cell system in which experiments can be performed to measure chemical and physical changes as the liquid is isothermally stressed, and the evaluation and development of instrumentation techniques to analyze liquid- and solid-phase changes in hydrocarbon-based materials and to monitor particle formation and growth.

II. BACKGROUND

Thermal stability problems were first identified in the 1950s when fuel systems' temperatures were increased relative to the level in previous aircraft; engine failure occurred due to fuel nozzles being plugged with deposits from fuel degradation (Jonke and Nelson, 1955). Until a more quantitative definition can be developed, thermal stability will be qualitatively defined as the [lack of] propensity for a fuel under a thermal stress to form insoluble solids and deposits on surfaces. A fuel that forms relatively little sediment and deposits under conditions of thermal stressing is considered to have high thermal stability. As aircraft have attained higher speeds and correspondingly experienced higher temperatures, fuel degradation and deposition have increased. Fouling of nozzles, manifolds, filters, injectors, and heat exchangers has been observed. Recognizing that fuel thermal stability in both commercial transports and military aircraft is an important safety and performance concern, the military services and industry have been investigating thermal stability problems since the 1950s.

The degradation of aviation fuel and subsequent solids deposition involves coupled chemical and physical processes. A brief review of investigations and experimental techniques pertinent to these processes is presented here. More complete reviews of the literature are available on fouling (Epstein, 1978; Somerscales and Knudsen, 1981) and on thermal stability of aviation fuels (CRC, 1979).

Studies of fuel thermal stability have been performed using a variety of experimental apparatus to investigate the chemistry of fuel degradation and to investigate the sensitivity of a fuel's thermal stability to test parameters such as temperature, pressure, oxidative condition, metal surface type and roughness, fuel composition, flow rate, and time of exposure. See, for example, TeVelde et al., 1983; Marteney and Spadaccini, 1986; Taylor, 1974; Taylor, 1976;, Taylor and Wallace, 1967; Roback et al., 1983; Clark and Thomas, 1988; Vranos et al., 1981; and Bol'shakov, 1972. Investigations of both long-term storage stability and short-term in-flight thermal stability have been performed; this program is concerned with problems of in-flight thermal stability. Experimental apparatus used to investigate the thermal stability of jet fuels have ranged from small-scale devices to large, fuel-system simulators. The evolution in testing has been summarized by the Coordinating Research Council (CRC, 1979). Research into fuel thermal stability has predominantly used small-scale flowing systems. Testing with fuel-system simulators has been limited because of the expense involved.

Both static and dynamic (flowing) heating tests have been performed using small-scale devices; dynamic tests are generally considered to be more representative of the actual environment a fuel will experience. However, because a dynamic test incorporates coupled fluid dynamics, heat transfer, mass transport, and chemical kinetic processes, which all can affect the deposition process, the interpretation of data from such tests is difficult. Data from such studies often lead to inconclusive or contradictory results. As indicated above, numerous flow studies have been performed to investigate the effects of various parameters on deposition rate. The general system design usually has fuel, sometimes preheated and filtered, flowing through a metal tube or over metal coupons in a heated environment. (Although model compounds would simplify the chemistry involved, few tests have been run using highly purified model compounds because of the high cost; flow experiments require a relatively large volume of fluid.) The parameters measured during the test are generally flow rate, temperature, and pressure. After the test has been run for a specified time interval, the tube through which the fuel flows is removed and the amount of carbonaceous deposits on the tube, or section of the tube, are determined. The wall temperature is generally correlated with the mass of deposit formed at that wall location. The lack of detailed measurements of changes in the fluid and solid phases has hindered the determination of the primary parameters, or coupling between parameters, that affect fuel deposition.

A number of specification tests have also been developed, with the most common dynamic specification test currently being the Jet Fuel Thermal Oxidation Tester (JFTOT), ASTM Method D3241 (ASTM, 1977). The JFTOT specification test is designed to evaluate the acceptability of a proposed fuel sample based on the discoloration of an aluminum tube on which deposits are formed and on the filter pressure drop due to fouling. The degree of tube discoloration is assumed to be directly proportional to the amount of deposit on the tube. In the standard operation of the JFTOT test, fuel is flowed over a tube at a flow rate of 3.0 mL/min for 150 min at a fuel system pressure of 3.45 MPa (500 psig). In the JFTOT test, the tube temperature is controlled, rather than the fuel temperature. Commercial, and most military specifications, require the test to be run at a maximum tube temperature of 260°C. The filter pressure drop can be quantitatively measured. The discoloration on the tube due to the formation of deposits can be determined visually by comparison with the ASTM Color Standard or by using a Mark8A Tube Deposit Rater (TDR), based on a light reflectance technique. Individual fuel specifications indicate whether the fuel sample has passed the JFTOT test.

The JFTOT apparatus has deficiencies both as a specification test and as a research tool. The relevance of the operating conditions to actual flight conditions is questionable because the time that a fuel is exposed to the high test temperature is much longer than in a fuel system. Conditions were made more severe in the JFTOT test to accelerate fuel degradation. The flow rate was set to ensure laminar flow and thereby simplify the flow profiles; however, transitional or turbulent flow may exist within an aviation fuel system. Recent numerical analyses (Oh et al., 1989) have shown that even the laminar flow assumption may be incorrect. Additionally, the TDR technique to rate the tube discoloration does not recognize some deposit colors and therefore comparisons between different tests may be questionable. Although not designed as a research tool, the JFTOT apparatus or modifications of that design have been used as such. These apparatus cannot generally produce quantitative information regarding deposit characteristics or the local conditions that cause deposits to occur. The flexibility in operating conditions and the ability to make local measurements of temperature, pressure, gas composition, liquid composition, and solid composition is very limited. Generally, these tests only monitor wall temperature and an area-weighted average mass of deposits formed over a determined time interval.

Because of the lack of experimental apparatus and instrumentation required to measure the coupling of the various fluid dynamics, heat transfer, mass transport, and chemistry processes occurring simultaneously in an aviation fuel system, research studies to investigate fuel degradation and deposition formation have been hampered. Data acquired in past static and dynamic tests have not been sufficient to develop physical models of the processes involved. Although models for fluid dynamics and heat transfer have been developed in other fields, the complexity of the fuel chemistry and the effects of these processes on solids formation and deposition have resulted in little quantitative information on the kinetics of solids formation and growth as fuel is thermally stressed. Without this information, reliable predictions of fuel performance cannot be made.

A substantial amount of experimental work has been performed using both static and dynamic tests to investigate the chemistry of deposit formation and the effects of system parameters such as temperature, oxygen pressure, and surface metal on deposit formation. It has been generally concluded that, although a fuel may be composed of several thousand components, the minor trace components and contaminants are of major importance in determining the stability of the fuel (CRC, 1979). The overall chemistry of fuel degradation follows a mechanism of hydrocarbon autoxidation. In the initial step of the autoxidation mechanism, a hydrocarbon forms an alkyl free radical. Propagation steps of the reactive free radical form a stable product, a hydroperoxide. If sufficient oxygen is present, the hydroperoxide concentration reaches a limiting concentration where the hydroperoxides decompose. Alcohols and ketones are formed, followed by acids, hydroxyketones, and esters under more extensive oxidation. Although this general hydrocarbon autoxidation mechanism has been supported by a number of researchers (see e.g., Mayo, 1968; Scott, 1965; and Emanuel et al., 1967), and more detailed mechanisms developed for jet fuels or fuel surrogates (Hazlett et al., 1977; Reddy et al., 1988; Bol'shakov, 1972), kinetic expressions for the process have generally not been developed. This deficiency in quantitation makes comparison of work between various researchers difficult.

Numerous studies have examined the effect of composition on fuel degradation and have shown the importance of trace elements and contaminants. See, for example, Taylor, 1968; Taylor, 1976, Reddy et al., 1989, Bol'shakov, 1972. Nitrogen and sulfur compounds, even in small concentrations, can significantly increase the amount of deposit formed. However, different nitrogen- and sulfur-containing compounds can have vastly different effects with some compounds not affecting the deposition process and some even inhibiting deposits. The results are indicative of the complexity of the chemistry. Studies have also shown the sensitivity of formed deposits to trace amounts of metals present, especially copper, iron, zinc, and lead (CRC, 1979).

The most important parameter affecting the amount of deposit formed under given conditions is generally the oxygen concentration. Numerous studies have shown that deoxygenation of fuels markedly improves stability in the oxidative regime that current fuels generally encounter. See, for example, Taylor and Wallace, 1967; Taylor, 1974; Watt et al., 1968. However, studies on a spectrum of fuels indicated that, although deoxygenation has the potential for a marked reduction in deposit formation, other aspects of the fuel composition are also important in determining the degree by which deposit formation is decreased.

Although these investigations have shown how changes in operating conditions and fuel composition qualitatively affect the solids deposition process, models that can predict this behavior have not been forthcoming. Because slight variations in a fuel's composition can significantly affect its deposition rate, and quantitative models for these processes are not available, a priori predictions of a given fuel's thermal stability cannot be reliably made. The lack of adequate experimental apparatus and instrumentation to monitor the many parameters affecting fuel thermal stability in a heated, flowing system has made the acquisition of data required for model development difficult. Indeed, because of these deficiencies, quantitative measures of the performance of fuels as determined by the specification tests (e.g., the JFTOT) are not possible. To accurately assess fuel performance and aviation fuel system safety, quantitative models of the physical processes affecting fuel degradation and deposit formation must be formulated. A prerequisite is that apparatus and instrumentation be developed to obtain data necessary for the model development, calibration, and validation.

III. APPROACH

The program objective addressed in this report is the development of the capability to predict the thermal stability of a specified hydrocarbon fuel under given operating conditions and a given system geometry. Prediction of the thermal stability of a fuel in an aviation fuel system requires mathematical formulations (models) for the fluid dynamics, heat transfer, mass transport, and chemical kinetics of the system. General mathematical models for fluid dynamics, heat transfer, and mass transport are well established; however, values for the model parameters specific to the system under consideration must be determined. Mathematical models for the chemical kinetics of jet fuel degradation and deposition processes are not available. These models will be formulated from experimental data and must be simplified sufficiently to make the numerical solution of the coupled equations practical. As mathematical models are developed, computer codes containing these models will be developed and calibrated. These computer codes are anticipated to be used to support aviation fuel system design by predicting where potential fuel deposition problems might occur. Other uses include evaluation of the performance of candidate fuels, design of experiments, and data interpretation.

Figure 1 shows a representation of the processes that can occur in a flowing system of heated hydrocarbon fuels that result in solid formation and deposition on a surface. Krazinski and Vanka (1989) give a brief summary of possible processes involved in solid deposition from jet fuel. The fluid dynamic regime of the fuel may be laminar, transitional, or turbulent. As the flowing fuel is stressed by an external heat source, the hydrocarbon fluid degrades and solid particles form and grow. Particles formed within the bulk liquid will be transported primarily by convective and diffusive forces. Secondary processes accounting for mass transport to the surface may include thermophoresis, electrostatic interactions, inertial impaction, and gravitational settling. Particles that approach the surface may adhere and form a deposit. The mechanisms by which the

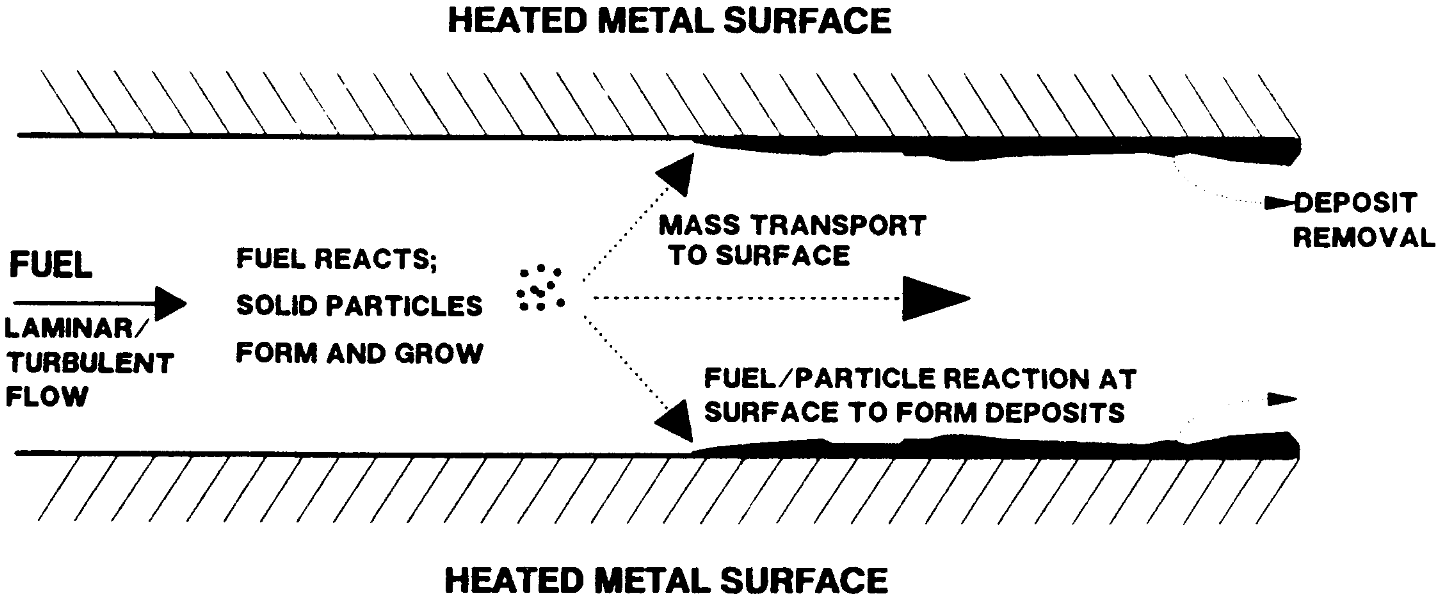

Figure 1. Schematic of Jet Fuel Deposition Processes.

particle attaches to the surface will depend upon the physical and chemical characteristics of the surface and the corresponding interactions with the particle. Particles may also form at the surface. The deposits may change with time because of the conditions at the surface. As the solid mass accumulates, parts of the deposits may be removed and flow downstream. These removal mechanisms are expected to vary with flow conditions.

The least understood processes are associated with the chemical degradation of hydrocarbon-based fuels under thermal stress, the formation and growth of particles, the reaction of the particles or fuel near the surface to form deposits, and reactions on the surface itself to alter the characteristics of the deposits. Therefore, the approach for the early stage of this program is to isolate the various chemical processes and develop mathematical formulations describing those processes. Models will be developed that can predict the reaction of hydrocarbon-based fuels under a thermal stress to form solid particles, the growth and reaction of those particles, the process by which the particles adhere to the surface and form deposits, and the reactions, if any, of the deposits on the surface itself. The program will attempt to determine global kinetic expressions for fuel degradation and solids deposition based on changes in concentration of compounds or functional groups that are known to be important in the autoxidation mechanism. When these models are formulated, dynamic tests will be performed to determine the importance of the various mass transport mechanisms, the parameter values for the flow, heat transfer, and mass transfer models, and the coupling between the chemical processes and other processes occurring in the flowing system.

The first step in the model development is the identification of processes and parameters relevant to fuel degradation and solids deposition in a heated, flowing system. Section IV of this document, "Process and Parameter Identification," discusses the processes that have been considered and the parameters that must be measured or estimated to formulate the coupled fluid dynamics, heat transfer, mass transport and chemistry model. The second step in the model development is to obtain the means to measure the data required for model development and evaluation. The chemistry of the fuel degradation and solids deposition processes will be investigated in the initial stages of the program. The development of experimental apparatus in which to perform these kinetic experiments is described in Section V. Preliminary characterization studies of the apparatus are described. In conjunction with this development, instrumentation required to monitor the selected parameters has been evaluated and developed for integration with the experimental apparatus; the discussion of this instrumentation can also be found in Section V. Data are reported that were obtained during the evaluations. The development of the experimental system is not yet complete; when completed, experiments will be performed to develop the chemistry models. These experiments will be designed to decouple flow, heat transfer, and mass transport processes from the chemistry. Section VI discusses results from preliminary numerical analyses performed to support the identification of important parameters and to provide benchmark calculations by which numerical models developed by this program may be partially verified. Section VII presents a summary of the work performed in the first year of this program. Plans for the second year of this program are discussed in Section VIII.

IV. PROCESS AND PARAMETER IDENTIFICATION

Prediction of the thermal stability of jet fuels requires models for fluid dynamics, heat transfer, mass transport, and chemical processes. Processes that are expected to occur were briefly mentioned in a previous section. Qualitative descriptions of these processes suggest the types of data that need to be measured to develop quantitative models; however, specific data parameters cannot always be specified a priori. Previous research on fuel thermal stability indicates that the formation of sediment and deposition of solids depend highly on the chemical processes involved. Knowledge of the liquid degradation, particle formation, and particle growth processes indicate that data should be obtained on the changes in chemistry in the liquid phase, on the changes in the chemical and geometrical characteristics of the formed solid particles, and on the quantity and chemical characteristics of solid deposits formed on the surface. Changes in the gas-phase composition should also be monitored. As discussed in Section VI, preliminary numerical sensitivity analyses suggest that fluid velocity and temperature can have a significant effect on solids deposition and should be tightly controlled. The analyses also suggest that kinetic parameters must be well known to accurately predict deposition rates, which supports the decision to concentrate on the development of the chemistry models for this system. This section discusses the various processes that are expected to occur and the specific parameters that appear to most significantly affect the formation of sediment and the deposition of solids. These conclusions are based on previous investigations (as described in Section II) and on results from preliminary sensitivity studies (described in Section VI). Discussion is also presented describing how these processes might be modeled.

The flow regime of the liquid fuel has been shown to have a significant effect on the deposition rate (Roback et al., 1983, Marteney and Spadaccini, 1986, Krazinski and Vanka, 1989). The flow regime (laminar, transitional, or turbulent) affects both the temperature distribution within the fluid and the transport of particles. As expected, numerical analyses show that when flow is turbulent, the formation and deposition of solids are more sensitive to the velocity distribution. Various models of turbulence are available (e.g., a mixing length model and a k-ε model) and they contain constants that have been determined empirically to be valid over a range of flow conditions. Models are also required that predict removal of deposits from the surface due to fluid shear forces. Some constitutive models for deposit removal have been postulated (Epstein, 1978) but further development is necessary. Measurements of velocities within the flow field are required, as are the determination or specification of fluid property values, system geometry, and initial and boundary conditions relating to flow. Model parameters specific to each fuel must be determined through independent testing or calibration tests. The development of models to predict deposit removal may require particle tracking data.

Heat transfer processes include conduction, convection, viscous dissipation, and enthalpy changes due to chemical reaction. Models for these processes are well formulated, with the exception of the chemical reaction expressions. As expected, temperature is a primary factor affecting fuel degradation and solids deposition. As shown by numerical analyses (see Section VI), if an Arrhenius rate formulation can be assumed to describe kinetic rates, reciprocal absolute temperature is logarithmically proportional to the deposition rate. This suggests that the temperature should be tightly controlled and accurately measured during kinetic experiments. Requirements for solving the energy equations again include specification of fluid and solid thermal property values, the system geometry, and initial and boundary conditions.

Mass is expected to be transported primarily by diffusive and convective forces. Diffusion may occur by ordinary bulk diffusion, eddy diffusion, or Brownian diffusion. Models for these processes are available but the relative importance of each process is highly dependent upon the particular system. Diffusion coefficients can be measured or inferred from particle size distributions. Numerical analyses indicate that the value of the diffusion coefficient used could significantly affect the predicted solid deposition rate. Although a single-valued diffusion coefficient was used in the numerical analyses described in Section VI, a distribution of values is expected under experimental conditions because of the distribution of particle sizes formed (see Section V). Reaction and particle growth may yield a wide size distribution of particles that subsequently exhibit a correspondingly wide distribution of transport parameter values. Knowledge of the solid particle property values is also required.

The chemical degradation mechanisms of hydrocarbon-based fuels under thermal stress, the formation and growth of particles in the bulk fuel, the reaction of the particles with the surface, and the reactions of particles near the surface are poorly understood. Liquid-phase reactions at low temperatures (<~700°F) proceed by an autoxidation mechanism involving free radicals. At higher temperatures, degradation is by pyrolytic mechanisms. Dissolved oxygen in the fuel is a major contributor to the degradation of fuels. The presence of trace compounds in the fuel such as sulfur, nitrogen, and metals increase degradation. Although such qualitative information is available describing which factors are important in producing solids from thermally-stressed fuel, kinetic models of these processes are not available. Little information, even qualitative, is available concerning reactions near or on the surface.

The sensitivity of deposition rate to parameters in an assumed Arrhenius rate equation was investigated through numerical analyses. Because the concentration of precursors in the hypothesized model depends linearly on the oxygen concentration, the solid deposition rate also depends linearly on the oxygen concentration. As discussed previously, experimental data also show the importance of deposition rate on oxygen, although the functional dependence may not be linear (Taylor and Wallace, 1967). This suggests the need to accurately measure the concentration of molecular oxygen or oxygen containing functional groups in the liquid phase. As might be expected, the values of the activation energy and pre-exponential constant in the Arrhenius liquid-phase reaction rate also has a significant effect on the predicted solids deposition rate. This dependence is again nonlinear. To determine kinetic expressions, the concentrations of compounds or functional groups important to the fuel degradation, as well as temperature and pressure. Experimental investigations suggest that concentrations of hydroperoxides, alcohols, aldehydes, ketones, ethers, heteroatom-containing compounds, and other oxygen-containing compounds should be measured.

As discussed in the previous section, initial experiments will attempt to eliminate flow, heat transfer, and mass transport processes and focus on monitoring chemical processes. Velocity and temperature measurements will be made in the experimental apparatus to determine the effectiveness of isolating the chemistry. The concentrations of hydroperoxides, alcohols, aldehydes, ketones, ethers, and other oxidation reactants/products in the liquid phase as well as sulfur, nitrogen, and inorganic trace metal elements need to be measured. Because products in the gaseous phase often reflect the types of reactions occurring in the liquid phase, gas-phase species should be identified and measured. Total system pressure should also be measured. The formation of sediment in the liquid phase as a result of fuel degradation suggests that particle size distributions in the liquid phase need to be measured. To support the determination of liquid-phase reaction mechanisms and the reactions occurring on the surface, chemical and physical characteristics of the solid deposits and the sediment should be measured. Additionally, the actual accumulation of mass on the surface should be measured because it is the global variable to judge the extent of the fuel degradation/solids deposition process.

The following two sections describe the experimental apparatus that is being developed to perform experiments to support kinetic model development and the instrumentation techniques that have been considered to acquire data described above.

V. EXPERIMENTAL SYSTEM DEVELOPMENT

A. THERMAL STRESS CELL DEVELOPMENT

Isolation of the chemical processes from mass and heat transfer effects is necessary to develop kinetic models of the degradation and deposit-formation processes. An experimental system, referred to as the Thermal Stress Cell, has been designed to thermally stress a contained volume of liquid under controlled temperature and pressure conditions. The system was designed to provide isothermal heating of a liquid, thereby eliminating convective flow and providing a static flow field to study fuel degradation with minimal coupling of fluid dynamics and heat transfer processes. Instrumentation access, including access for optical techniques, was incorporated into the design. Preliminary tests have been performed to ascertain the capability of the system to provide isothermal heating. It is anticipated that a second-generation heating apparatus design may be required to provide adequate temperature control. This section describes the criteria used to design the apparatus, the various components that make up the apparatus, and data obtained from the evaluation tests.

1. Design Criteria

The objective was to design and build a vessel that can be used to study thermal stressing of jet fuels or other hydrocarbon liquids at elevated temperatures (1000 K) and pressures (1000 psi). Studies of both static and flowing test conditions are anticipated; however, initial designs would be for static tests. The static-cell tests will help characterize the liquid-phase fuel reactions and deposition mechanisms. Future flowing tests will provide data on the coupled fluid dynamics, heat transfer, mass transport, and chemistry processes, representing more realistic aircraft conditions. During the tests, measurements to accurately define the temperature and velocity distributions in the fuel, the chemical or physical characteristics of the fuel and the amount suspended solids will be made in the cell. For static tests, the velocity and temperature measurements will help define any natural circulation patterns induced by thermal gradients during both transient and steady-state heating of the fuel. For the flowing tests, velocity measurements will define the flow characteristics of the fuel as it passes through the heated region. Another criterion was that the cell must permit measurements of the chemical and physical characteristics of the liquid fuel, sediment, and solid deposits in situ using optical techniques and allow sampling of the fluid for external analyses. The first generation design attempts to include these criteria, keeping the basic design as flexible as possible.

2. Design Components

Based on the design criteria, two approaches were considered. The first approach consists of a single vessel that can withstand a combination of 1000 K and 1000 psia. Construction of the vessel is difficult because the structural integrity of mild steel, stainless steel, and most other metals are severely limited at these temperatures. Sealing and structural integrity could be compromised at high temperature and pressure conditions in this type of chamber. This design would also limit changes in the apparatus and the metals could be reactive with hydrocarbon-based fuels at these elevated temperatures. Based on these concerns, this design approach was eliminated.

The second approach considered incorporates an external vessel that can withstand the pressure and an internal thermal cell that contains and heats the fuel. There are numerous advantages to this type of design. First, construction of an outer vessel to withstand 1000 psia at lower temperatures (say 550 K maximum) is relatively standard. Second, the design lends itself easily to either flowing or static test conditions and, therefore, will not require a new design when test conditions change. Third, the construction material and configuration of the internal thermal cell can be easily changed. As will described later, the thermal cell could be a cube fabricated out of quartz but could easily be changed to a different material or geometry.

As shown in Figure 2, the Thermal Stress Cell consists of a pressure chamber, a thermal cell, and a heater assembly. To thermally stress a fuel, the liquid is loaded into the thermal cell which is then placed into the heater assembly. This assembly would then be placed inside the pressure chamber and appropriate instrumentation connected to the thermal cell, heater assembly, and pressure chamber. The pressure chamber would then be sealed and pressurized to a predetermined pressure. The fuel would be heated (either slowly or rapidly, depending upon the test conditions desired) to the desired temperature while data are continuously recorded.

A schematic of the pressure chamber is shown in Figure 3 and design drawings shown in Figures 4a-4d. The chamber is manufactured of SCH-160 pipe and has a maximum design pressure and temperature of 2000 psi and 550 K, respectively. Seven 7.6-cm diameter, 900 psi rate flanged penetrations are also available to facilitate optical, temperature and pressure measurements, power connections for heaters, inlet and outlets for the flowing tests, etc. The pressure chamber is designed to include five ports along the three orthogonal axes and two additional ports situated at angles of 30° and 45°, respectively, to one of the principal axes. This design provides for convenient and flexible optical access to the thermal cell. Optical measurements may be required at different angles and in three dimensions to allow full characterization of the fluid-dynamic conditions in the fuel and particle sizes. Because of the wide range of anticipated particle sizes, a range of angles for optical access was required for photon correlation spectroscopy measurements. See Section V,B. Successful application of this technique to a system containing an unknown distribution of particle sizes nearly always requires measurements at two or more scattering angles. For example, it has been shown (Bott, 1984) that even a simple bimodal distribution of submicrometer particles (91 percent by weight of 170-nm diameter and 9 percent by weight 822-nm diameter polystyrene latex spheres, respectively) can appear as a unimodal sample when examined only at a 90° scattering angle. Measurements at smaller scattering angles are useful for very dilute samples due to the substantial increase in scattering intensity. Moreover, the shape of the time-averaged scattering intensity vs. curve angle alone can contain valuable information regarding the particle size distribution and the presence of dust in the sample. Evaluations indicate that the design angles will provide suitable access. For optical measurements, the appropriate port penetrations will be flanged with quartz windows.

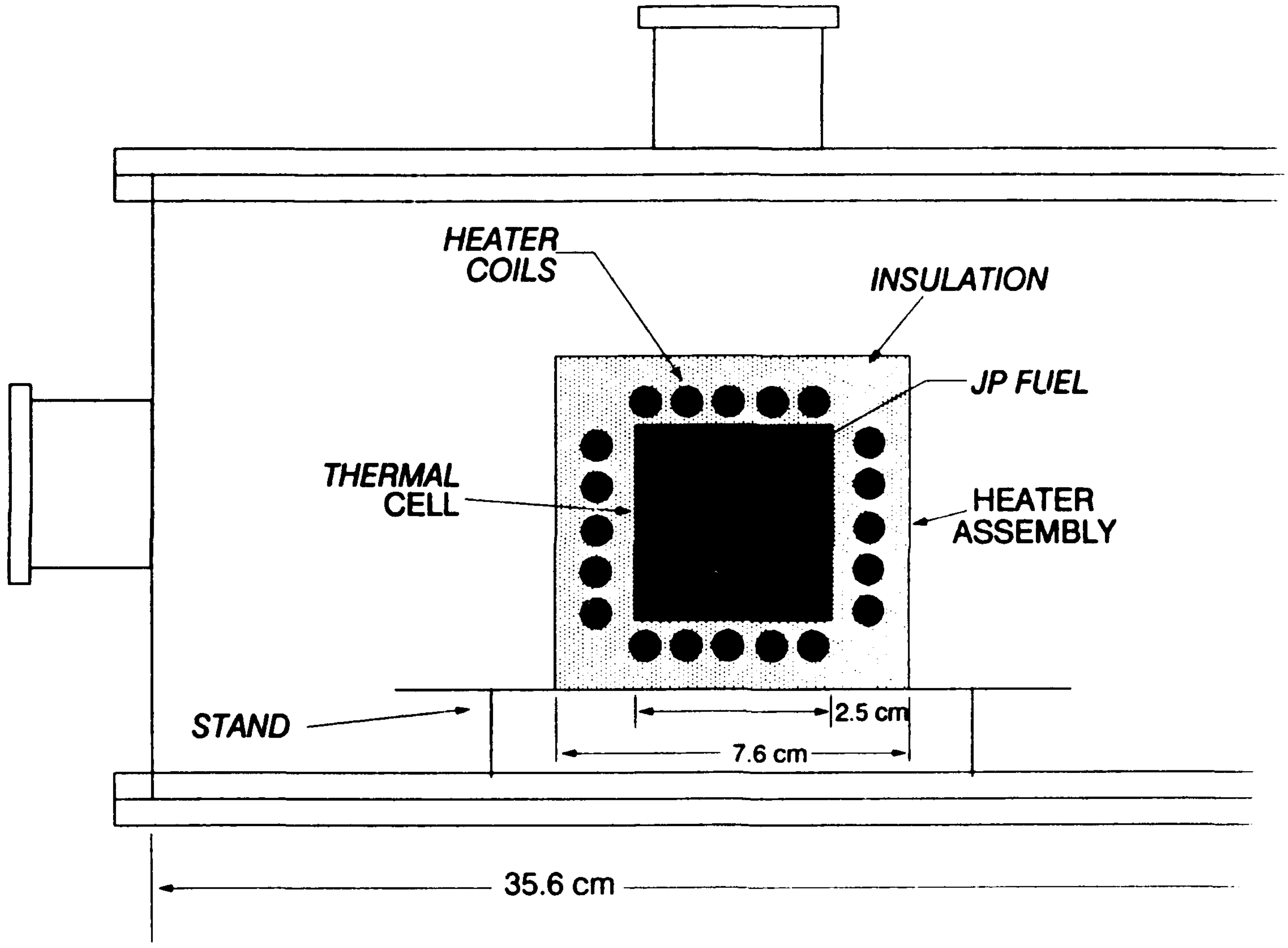

Figure 2. Schematic of Thermal Stress Cell.

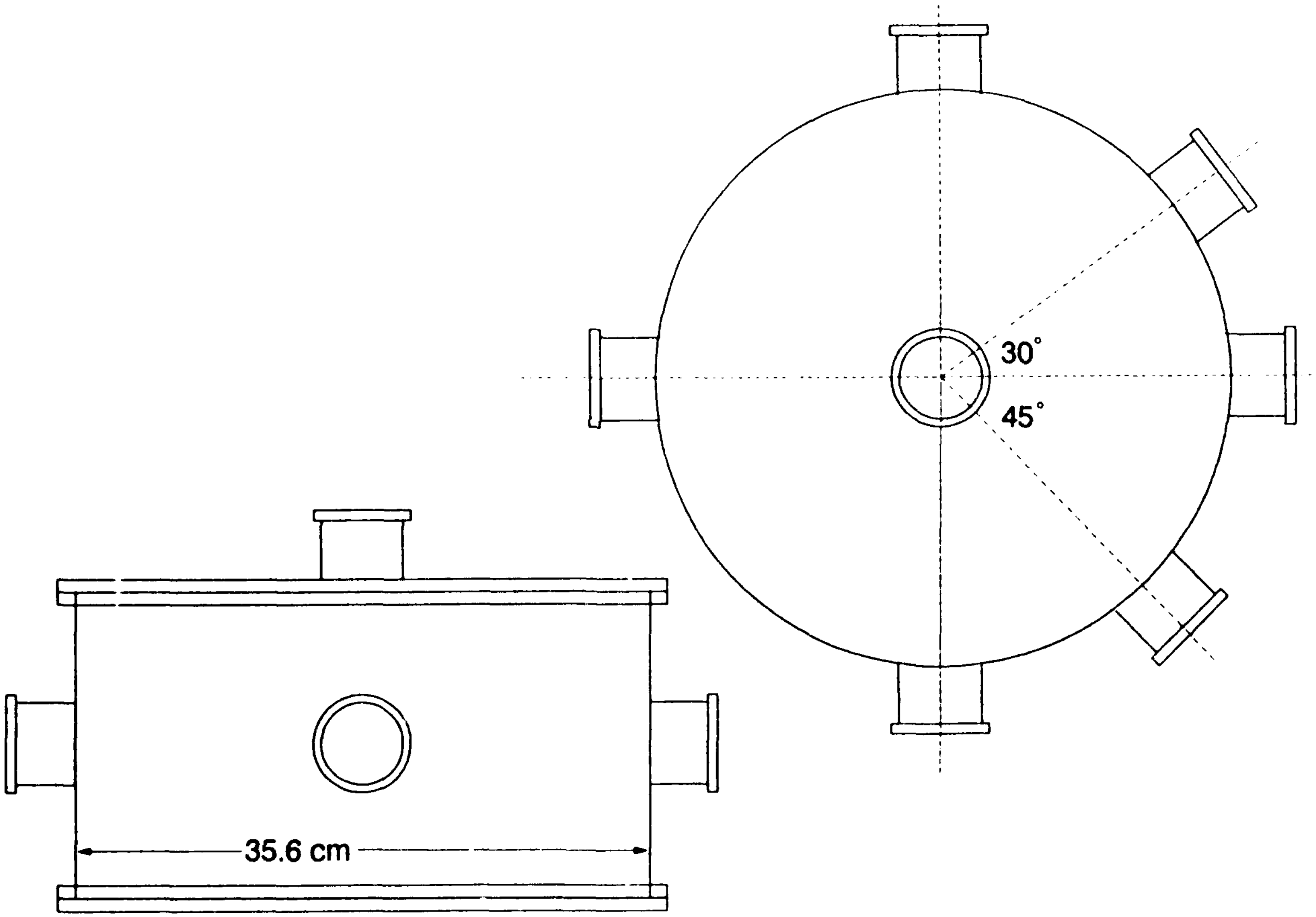

Figure 3. Schematic of Pressure Vessel.

PRESSURE VESSEL

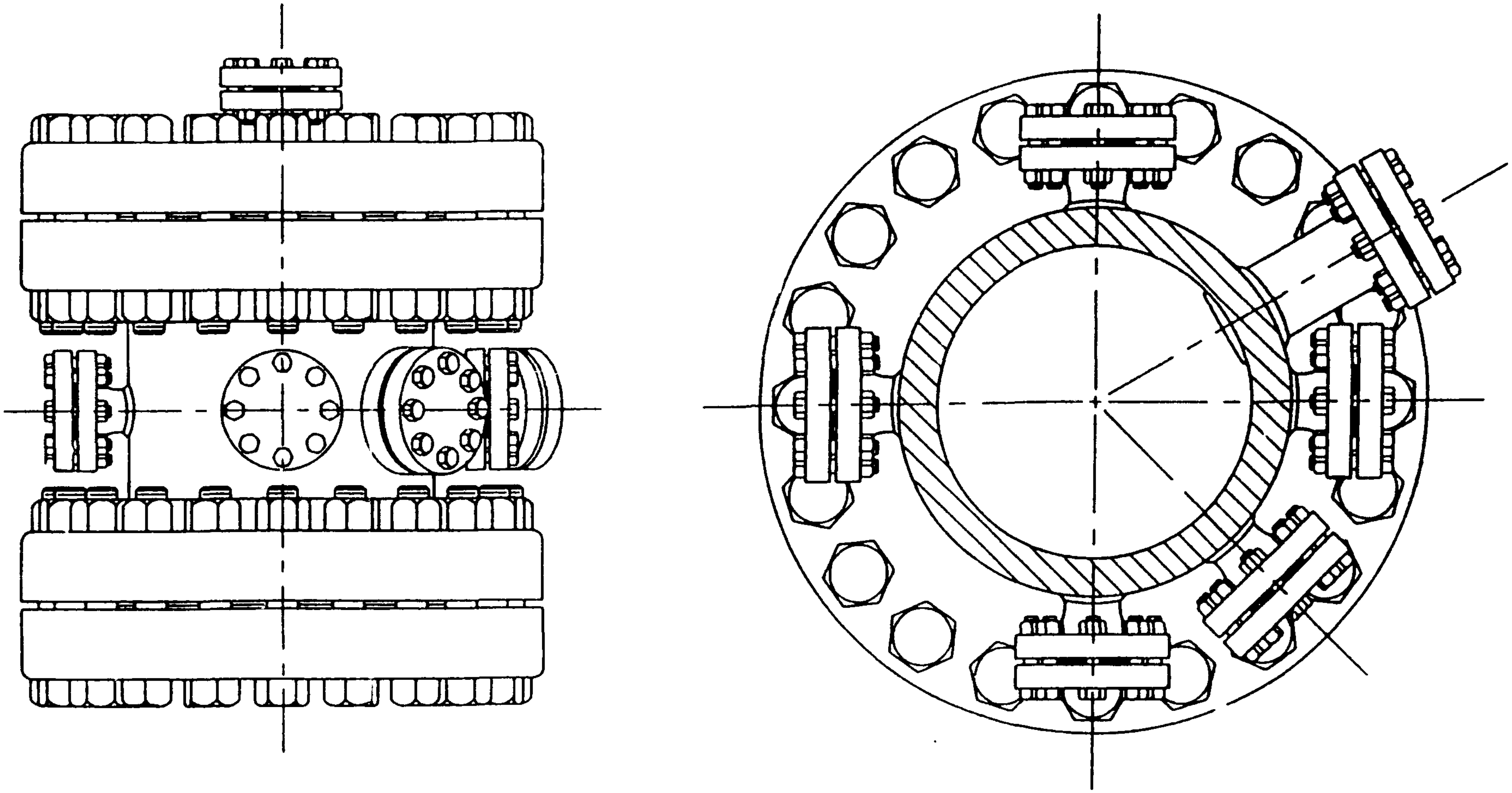

Figure 4a. Design Drawing of Pressure Vessel - Top and Side Perspective.

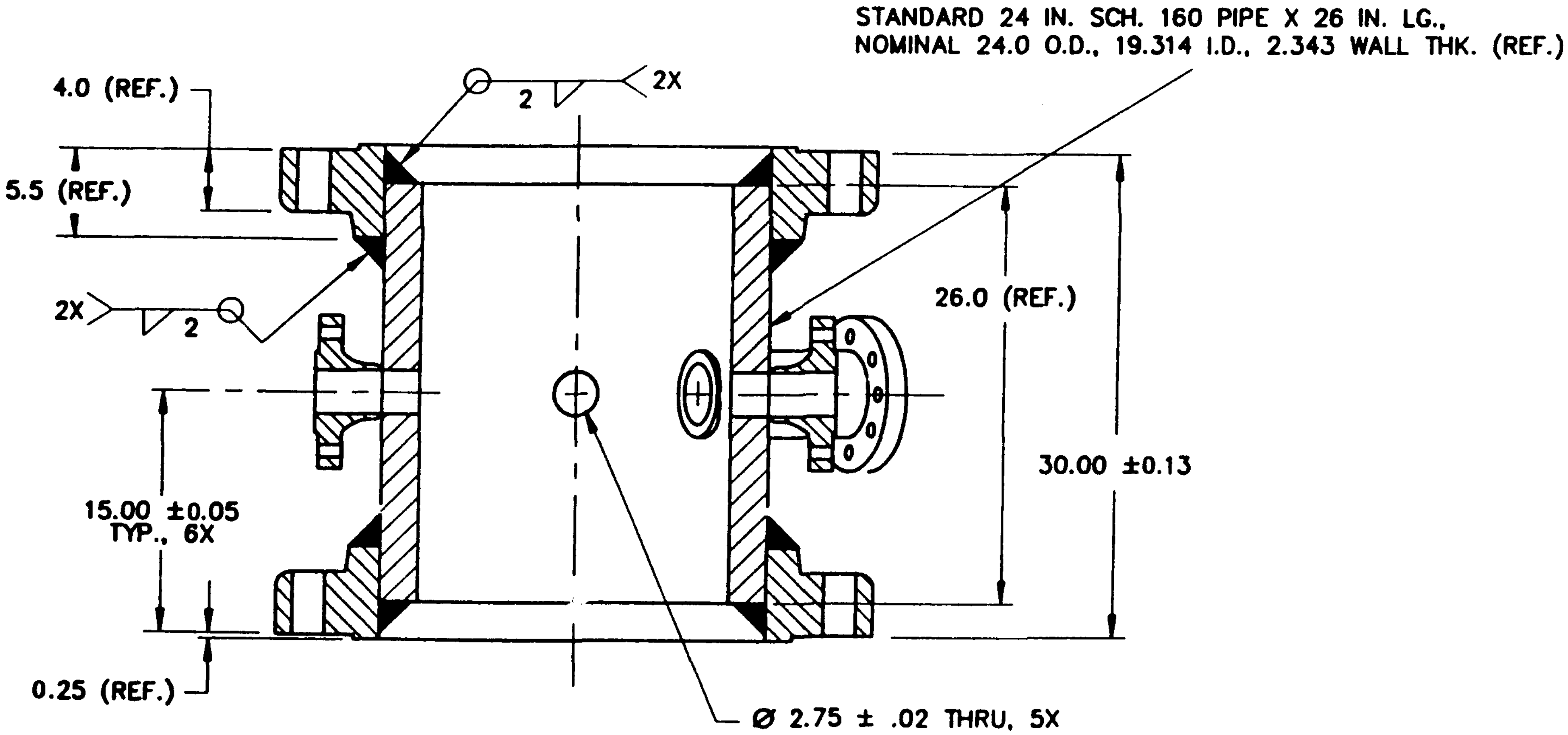

Figure 4b. Design Drawing of Pressure Vessel - Side View.

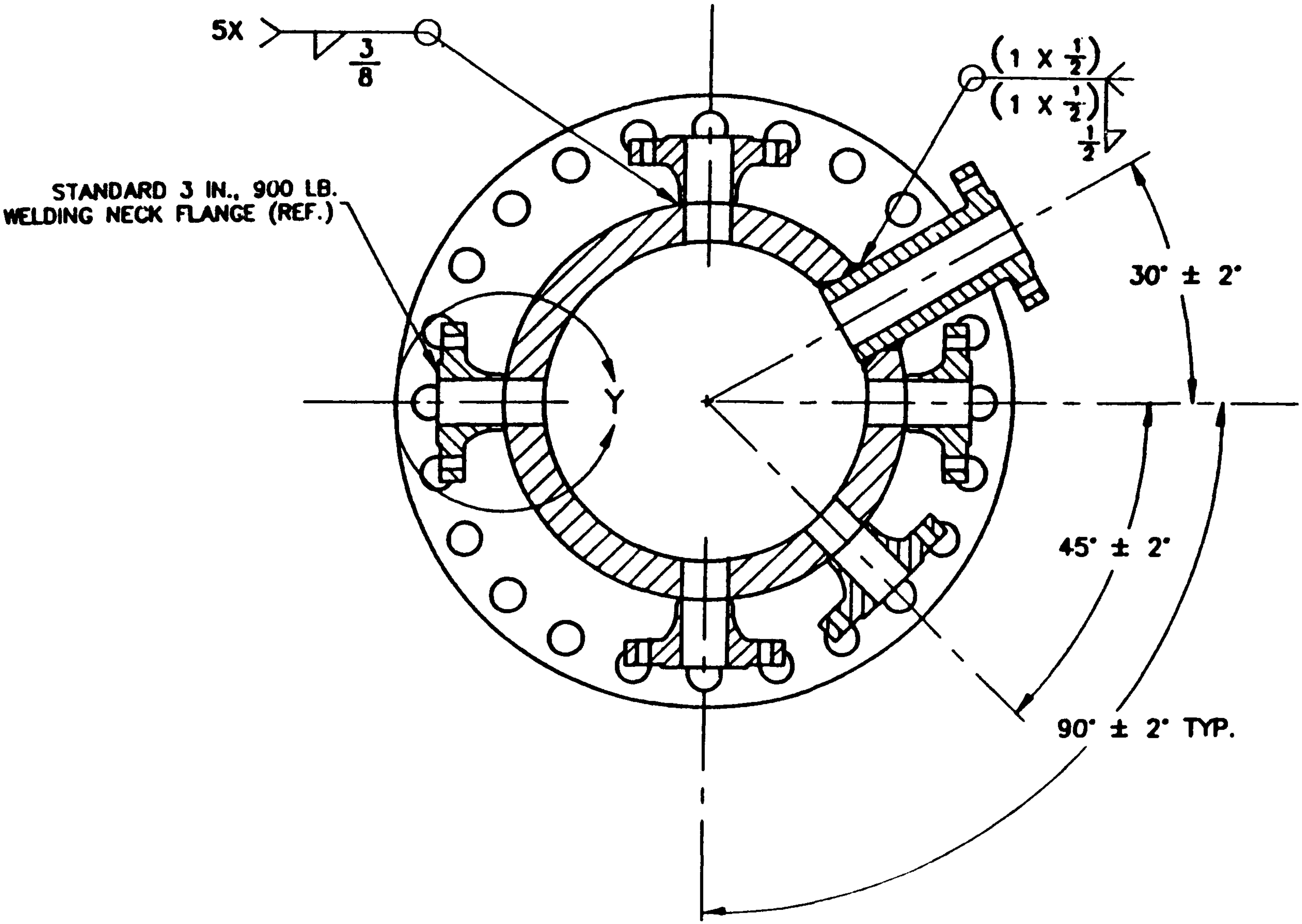

Figure 4c. Design Drawing of Pressure Vessel - Top View Showing Side Port Penetrations.

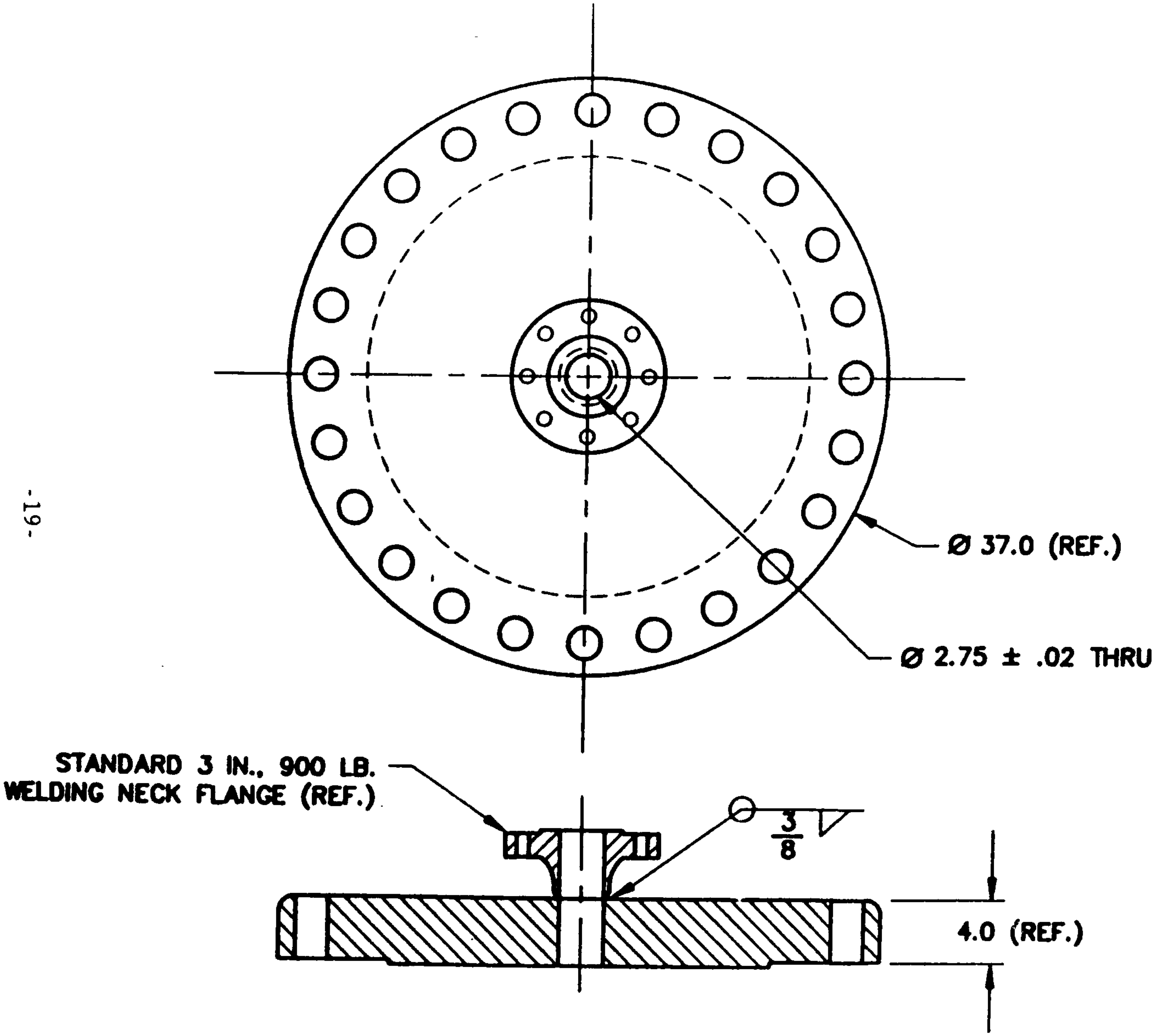

Figure 4d. Design Drawing of Pressure Vessel - Top View Showing Upper Port Penetration.

The thermal cell is designed to contain a specification jet fuel at temperatures up to 1000 K and is shown schematically in Figure 5. The first generation thermal cell is a 7.6(H) x 7.6(W) x 7.6(L) cm cube manufactured of quartz glass, yielding a volume of approximately 440 cm^3. A second-generation thermal cell has been fabricated with dimensions of 2.5(H) x 2.5(W) x 2.5(L) cm, resulting in a volume of approximately 16 cm^3. The top of the cube will be removable to allow fuel loading and removal. Additionally, small holes can be drilled into the quartz walls to allow liquid sampling during the testing; however, the first set of cells fabricated do not presently include this option.

The cubic geometry was chosen - as opposed to a cylinder - to enhance the laser-based measurement techniques. Optical measurements are facilitated by having the region of access perpendicular to the laser beam. However, cylindrical or octagonal cells may be used in future tests. Quartz was chosen because (1) the thermal cell is not a pressure boundary, (2) optical measurements are easily made through quartz and, most importantly, (3) quartz is relatively inert to chemical attack - even at 1000 K. The use of quartz will allow characterization of the thermal and fluid-dynamic conditions within the thermal cell without having to address chemical interactions between the fuel and thermal-cell walls. Moreover, after these baseline conditions have been defined, the effects of various metals/materials can be studied.

Quartz cubes have been successfully manufactured by a welding technique using quartz filler-rod. Additional cubes have been manufactured using a 'glue technique' developed at Sandia National Laboratories. The advantage of 'gluing' the cubes together is that the windows will not be distorted, as could occur during welding. Distortion of the quartz windows could affect the optical diagnostics.

The heater assembly has a cubic geometry and is designed to encapsulate and heat the thermal cell. The heater assembly for the cube 7.6-cm on a side will be approximately 10.16-cm on a side and will be manufactured of copper to minimize temperature distributions within the enclosure. The heaters are 800 W elements capable of heating the enclosure to temperatures of ~1200 K. As shown in Figure 6, the assembly is manufactured in two pieces which slide together around the thermal cell (i.e., a clam-shell design). Grooves are machined in the copper heater-plates to house the heaters and provide optimum heat transfer to the heater assembly and thermal cell (refer to Figure 7). To ensure that sufficient energy is available to heat the fuel to the desired temperatures, a heater is used on each side of the assembly. Furthermore, a highly-conductive diffuser plate is placed over the heaters to yield uniform heat fluxes to the thermal cell. The outside of the heater assembly is insulated with zirconia board (or similar insulation) to minimize heat losses to the surrounding pressure chamber. Also, the center of each heater plate has a 1.2-cm diameter slot approximately 2.5-cm long covered with quartz to provide the needed optical and instrumentation access to the thermal cell.

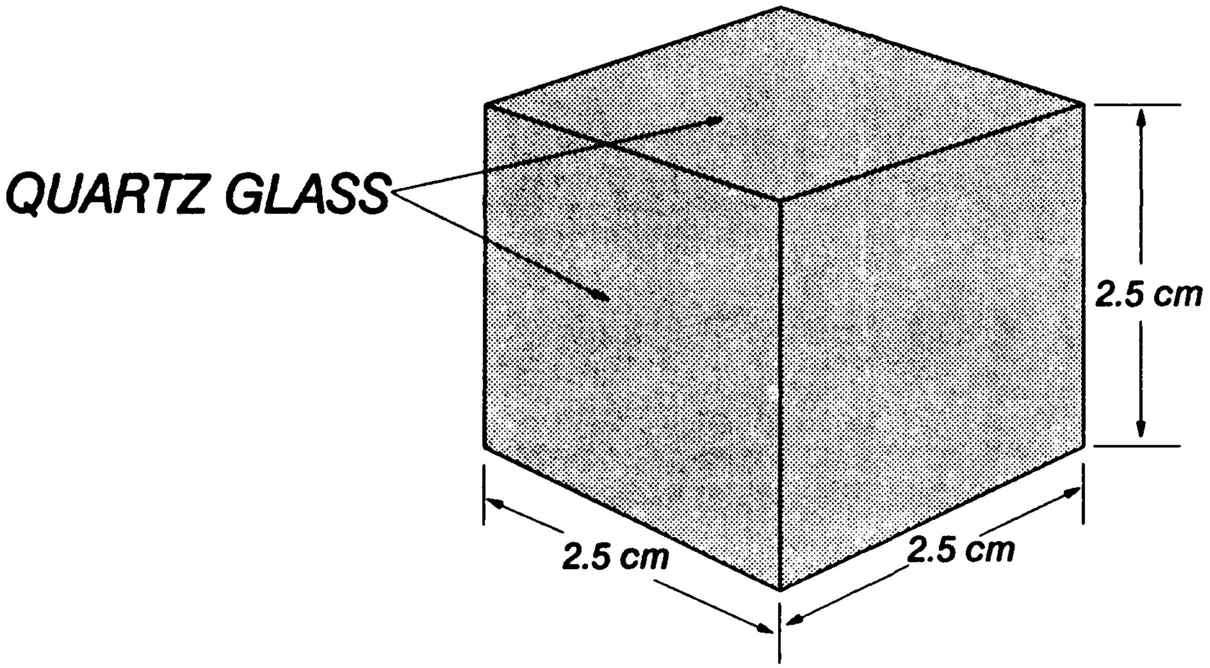

Figure 5. Schematic of Thermal Cell.

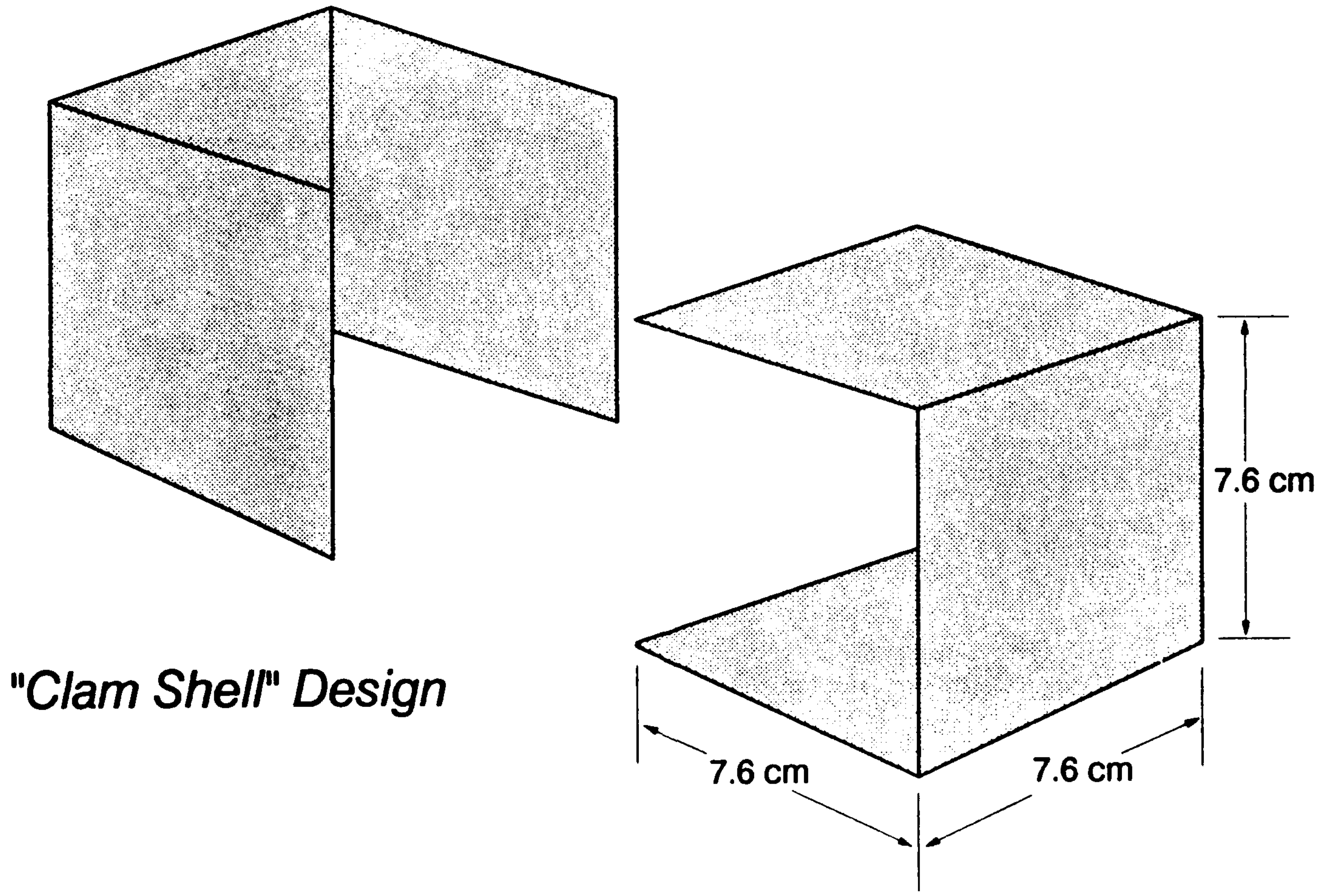

Figure 6. Schematic of Heater Assembly.

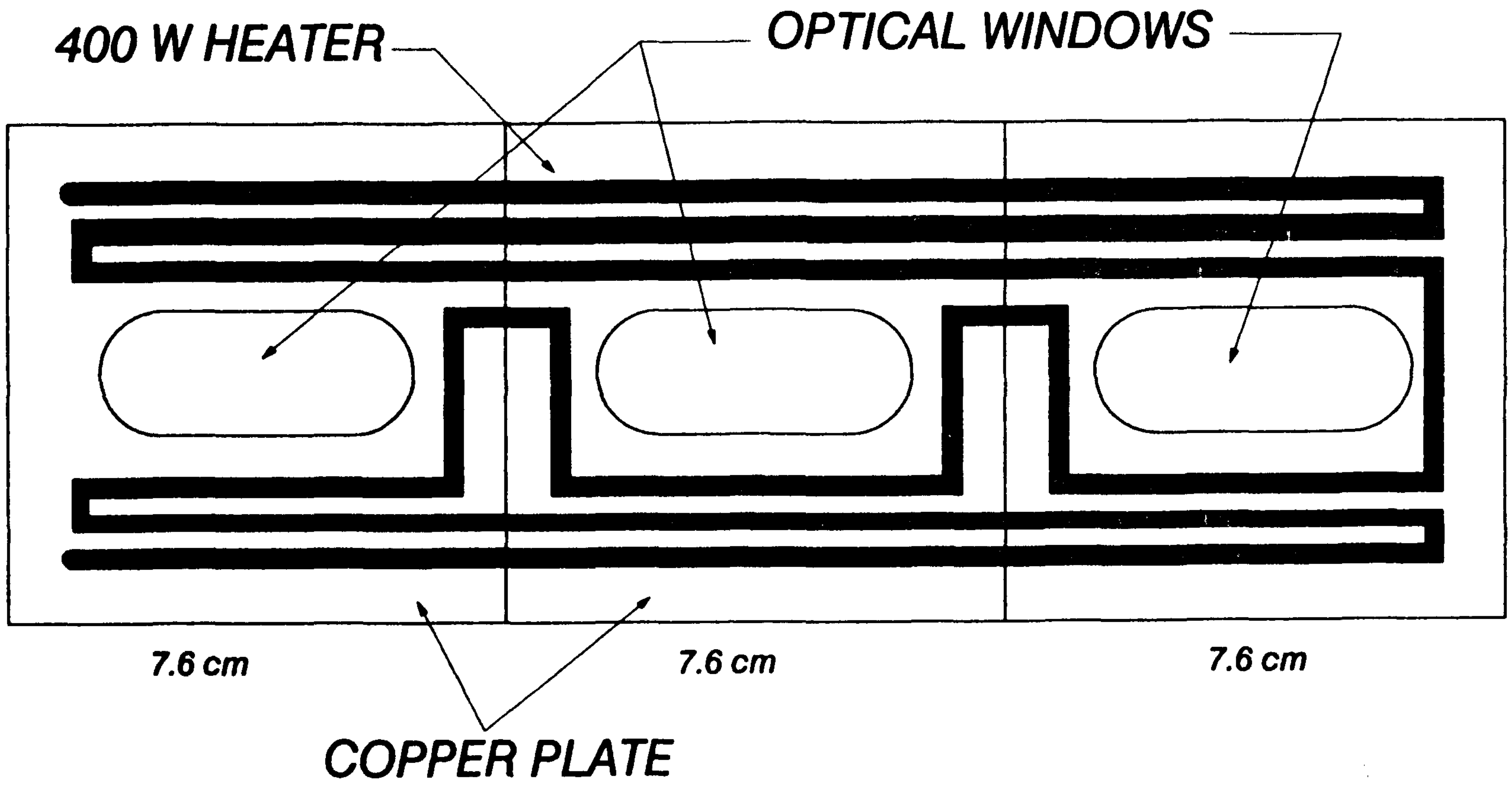

Figure 7. Schematic of Heater Groove Design.

3. Preliminary Cell-Characterization Studies

The internal quartz static cell and heater assembly is in operation and has undergone preliminary water-heating tests at ambient pressure to determine the capability to control fluid temperatures and convective velocities. Preliminary evaluation of its operational characteristics included examination of the heater wall and liquid bulk temperature uniformity and heating rate and was performed using the 440-cm^3 quartz thermal cell. The heater temperature is controlled in these preliminary experiments using Variac units. Thermocouples, both embedded in the test cell walls and used as liquid probes, provide local temperature data. The heater wall and liquid heating rate and maximum temperature for various electrical power inputs (Variac settings) were determined, and laser Doppler velocimetry (LDV) was applied for measurement of the convective velocity. Preliminary LDV measurements indicate that the convective flow increases with temperature. See Figure 8. This behavior was expected since wall heating will cause convective flow. The magnitude of the convective flow will be minimized by reducing the test volume, as planned for future tests. As expected, the liquid temperature lags wall temperature. See Figure 9. Use of a smaller liquid volume will allow faster heat up, as will better wall insulation. Tests to date have been performed at relatively low heater power levels. Window condensation initially limited applicability of the noninvasive diagnostics, requiring addition of a dry nitrogen purge. The overall capabilities of the cell have been judged adequate based on the current information.

The external pressure vessel is currently being assembled. During the second year of this program, the completed Thermal Stress Cell system will be tested under a range of temperature and pressure conditions to determine its adequacy. An internal quartz cell of volume approximately eight times less than the current cell will be used to facilitate heat transfer. Design modifications will be made as necessary. Some instrumentation techniques, discussed in the next section, will be integrated with the Thermal Stress Cell for in situ data acquisition.

B. INSTRUMENTATION EVALUATION AND DEVELOPMENT

Model development for the coupled flow, heat transfer, mass transport, and chemical processes occurring in an aviation fuel system requires measurement of fluid velocities, temperatures, and physical and chemical characteristics of the liquid- and solid-phase reactants and products present during the fuel degradation and solids deposition process. Instrumentation techniques for measurement of these parameters were evaluated and developed for use in performing both static and dynamic tests of fuel stability. The techniques considered for evaluation, the techniques chosen to be used in these tests, and the rationale by which those techniques were chosen are described in this section. Because the initial focus of experimental activities is on the development of models of the chemical processes involved in fuel degradation and solids formation

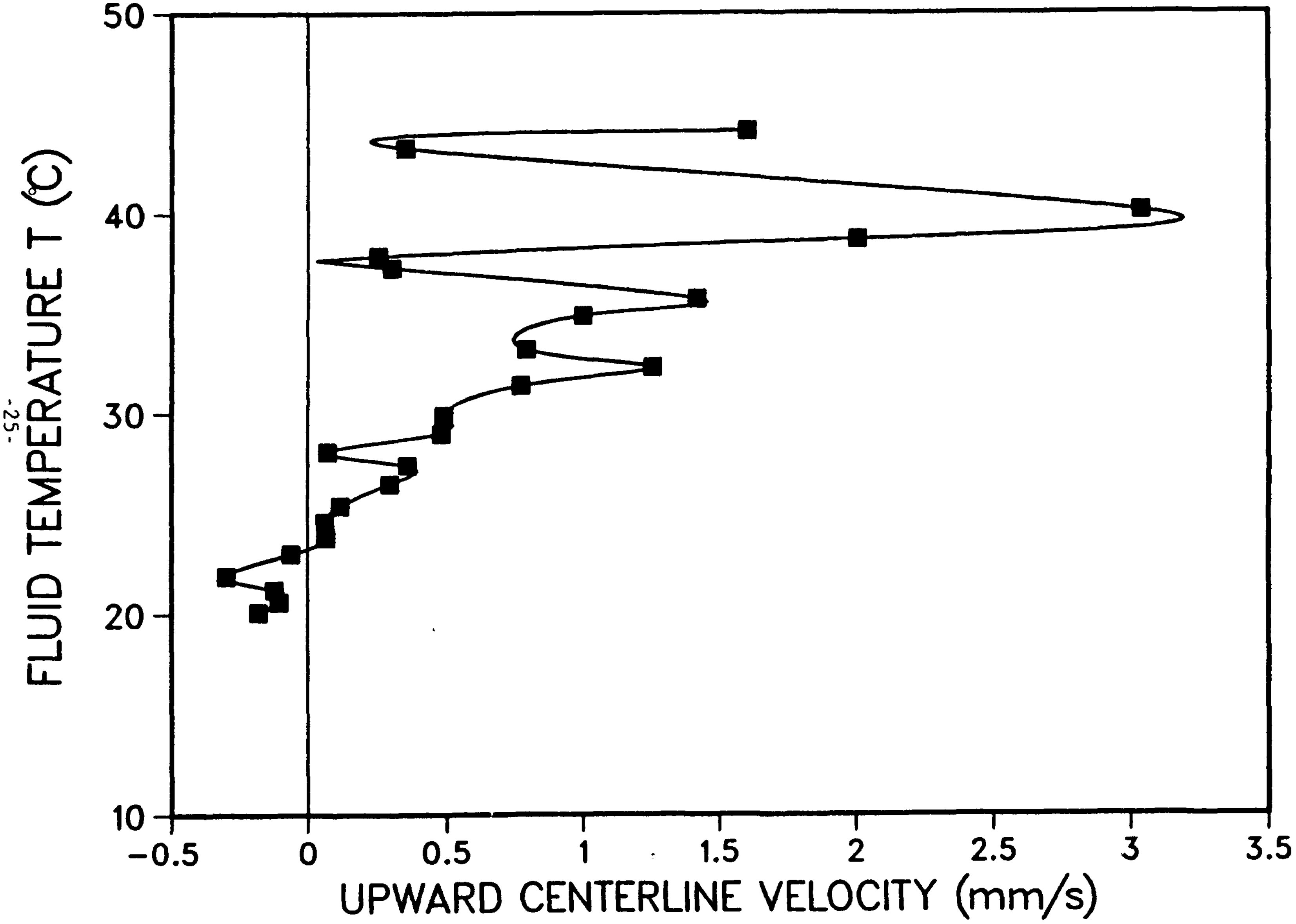

Figure 8. LDV-Measured Convective Flow in Heated Test Cell.

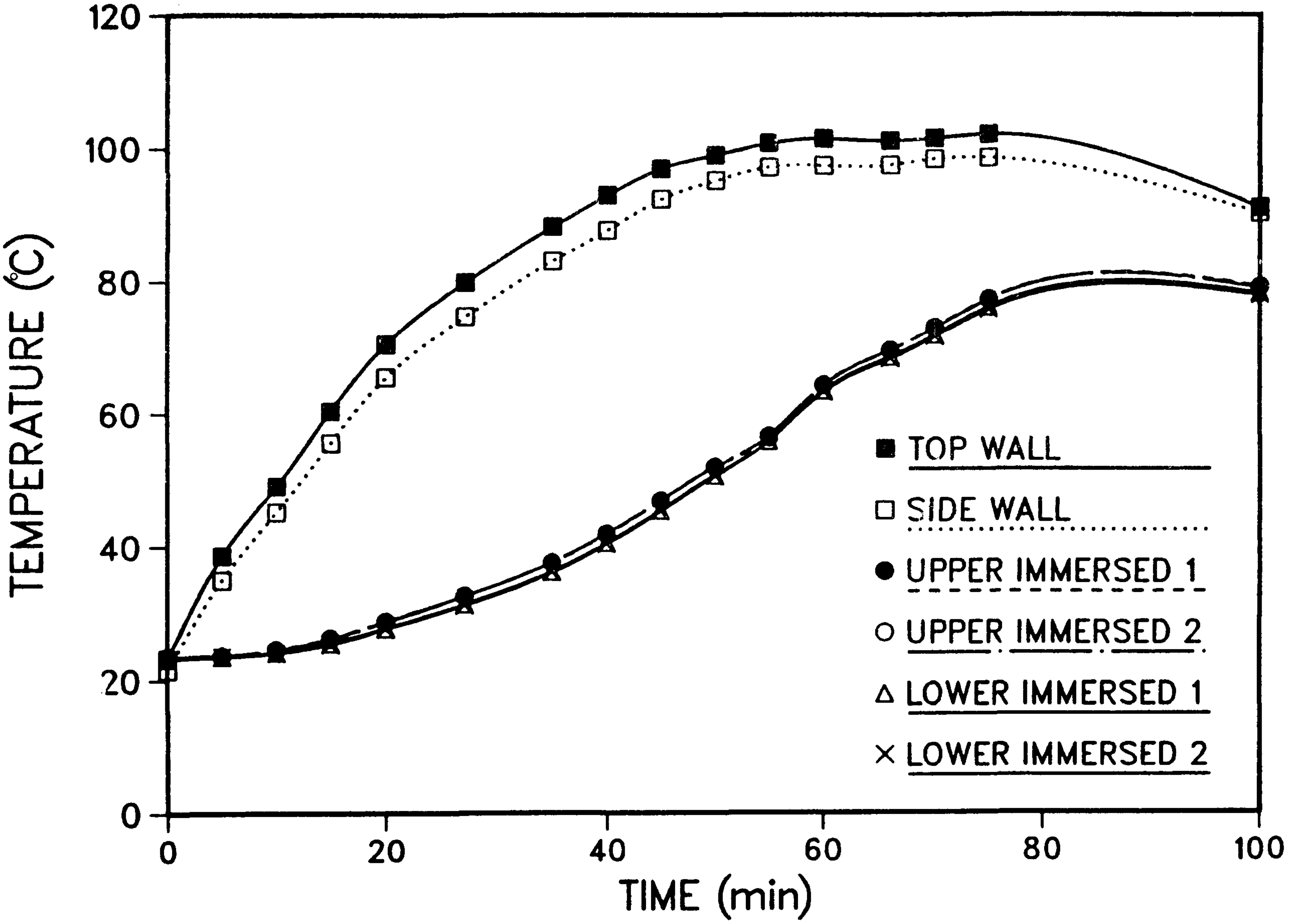

Figure 9. Typical Test Section Temperature History.

and deposition, and because the techniques for measuring velocities and temperatures are relatively well established, evaluations concentrated on techniques that would support data acquisition related to development of chemistry models.

1. Velocity-Measurement Techniques

Detailed fluid velocity measurements will be needed to characterize the flow conditions during fuel stress tests, and for code input and validation. Laser Doppler velocimetry (LDV) is a standard, noninvasive technique used to determine fluid velocity by measuring the frequency of the Doppler-shifted light scattered by seed particles suspended in the fluid. Mean velocities from several μm/s to over 300 m/s can be measured with up to 0.1 percent accuracy, and negative velocities typical of turbulent fluctuating flows can also be measured by applying frequency shifting. Full turbulence statistics are easily measured. LDV measurements have excellent spatial resolution; the spheroidal measurement volume has major and minor diameters of the order 0.5 mm and 0.02 mm, respectively. LDV measurements can be performed in strongly heated fluid; however, temperature gradients in the fluid can displace the measurement volume, effectively generating a larger measurement volume and introducing uncertainty as to its precise location.

Thermal or hot wire anemometry is a technique in which the convective heat transfer characteristics of a heated wire in the fluid are measured to determine the flow velocity. Typical configurations measure the current required to maintain the wire at constant temperature, with the current signal directly proportional to the fluid velocity. Wire dimensions are typically 5-μm diameter by 1-mm long, so the flow disturbance is often insignificant. For liquid measurements, the fragile wire is usually replaced by a hot film probe consisting of a conductive metal film deposited on a rugged quartz substrate.

Particle velocimetry (PV) is another technique that may prove useful. In this technique, neutrally buoyant tracer particles are placed in the flow, and their motion tracked over a known time period using pulsed light sheets. This technique is noninvasive and provides full-field velocity measurements (unlike the "point" measurements in LDV or hot wire anemometry). PV is limited to measurement in 2-D flows, since out-of-plane particle trajectories cannot be measured. Measurements of 3-D flows can be made using perpendicular light sheets, with digital correlation of object motions to determine the full flow field. PV is applicable in strongly heated fluids, even if large temperature gradients are present.

All of these velocity measuring techniques are fairly standard; the LDV and hot wire anemometry capabilities currently exist at Sandia National Laboratories. During the initial set of kinetic experiments to be performed, where the velocity and temperature gradients will be near zero, LDV is recommended as the technique for use in making velocity measurements. This technique is noninvasive and has good resolution capabilities, which are necessary characteristics for determining if fluid velocities and convective cells have been eliminated in the kinetic experiments. Preliminary characterization of the experimental apparatus developed for these kinetic tests has been performed, utilizing LDV to determine fluid velocities as the apparatus is heated. See Section V,A. When flow experiments are initiated, the PV technique may prove more useful. Therefore, PV and hot wire anemometry will be retained for consideration for later applications.

2. Temperature-Measurement Techniques

Fluid temperature measurements are needed for characterization of the fuel environment during testing. Temperature measurements can be made using thermocouples, either attached to test cell walls or immersed as probes into the liquid. Thermocouple measurements are straightforward, inexpensive, and commonly used. Laser Raman spectroscopy has been demonstrated as an effective means of in situ point measurement of temperature in liquid samples (Pan et al., 1984). This technique measures the ratio of the Stokes and anti-Stokes Raman scattering to determine point temperatures to within several degrees Celsius. Extension of this technique to high-temperature experiments (above 65°C) may require some modification to the basic technique. Commonly used for gas measurements, application of this technique to fuel thermal stress tests may also be limited by particulate disturbance of the measurements. Laser interferometry is another well-established method for noninvasive temperature measurements. Density contours are recorded in the interferogram that are directly proportional to the temperature field. Interferometry is limited to measurements in temperature fields that vary in only one or two dimensions. All fuel thermal stress tests should be run with thermocouples in place on the test cell walls. Initial measurements with thermocouples have been made in evaluating the experimental apparatus to be used in the kinetic experiments. Interferometric and Raman techniques will be retained for consideration if the thermocouple probes should prove to be inadequate.

3. Chemical- and Physical-Property Measurement Techniques

Development of models describing the degradation of hydrocarbon-based fuels and the subsequent deposition onto surfaces requires that physical and chemical characteristics of the liquid- and solid-phase reactants and products be quantitatively measured. In considering different techniques, the criterion was that the parameter measured should be involved in the liquid fuel reactions or the deposition process. Currently, mass deposition rate is the parameter generally used to measure the extent of the process. See, for example, Marteney and Spadaccini, 1986; Roback et al., 1983; Vranos et al., 1981. For this program, techniques were evaluated that had the potential to measure particle formation and growth, transient deposit mass and thickness changes on a surface, and chemical compositions and characteristics of both the solid and liquid phases. The capability of the techniques to provide useful information are evaluated and recommendation made as to which techniques should be considered for future use. A formal analysis protocol has not yet been developed however.

Particle Size Measurements

The field of particle size measurements in liquids was examined in two parts: sub-micrometer particle sizing and sizing of particles larger than 1 μm. Bol'shakov (1972) indicates that particles formed in the jet fuel thermal degradation process may be in the 10- to 100-nanometer range. Techniques for sizing of such sub-micrometer particles include sedimentation, laser diffraction, light scattering, light attenuation, and photon correlation spectroscopy. Gravitational or centrifugal sedimentation techniques are invasive, requiring that a sample be drawn for analysis. The particle density must be known, and the results are given as equivalent spherical diameters. Diffusion effects can lead to error in measurement of small particles. Laser diffraction techniques are wavelength limited, restricting their lower measurable diameter to about 0.5 μm. Light scattering techniques require that the particle refractive index be known. For sub-micrometer particles, the signal-to-noise ratio is typically low. These techniques usually require detailed calibration. Light attenuation techniques also have limited signal-to-noise ratio for small particles, and coincidence effects can introduce error in the particle size measurements. Photon correlation spectroscopy (PCS), also known as dynamic light scattering (DLS) or quasi-elastic light scattering (QELS), may be the most suitable technique for noninvasive measurement of the small particles expected in fuel thermal stability tests. PCS measures the particle diffusion coefficient directly, which can be used to determine particle sizes in the 3- to 10000-nanometer-diameter range. PCS measures the time-dependent intensity of the scattered light signal caused by Brownian motion of the particles in the illuminated sample. Large particles produce low frequency oscillations in the scattered signal, and small particles produce high frequency oscillations. PCS has several attractive features: the mean diffusion coefficient or particle size of a suspension can be noninvasively measured in situ and without knowledge of particle properties (density, refractive index), no calibration is required, particle sizing is done noninvasively, and the measurements can be made fairly quickly (1 to 30 minutes). There are a few disadvantages: particle concentration is not measured since only ensemble light scattering is measured, limited shape information is provided on the particles, and the data analysis deconvolution is difficult for broad particle distributions. Because of limitations of the other techniques and the capabilities of the PCS technique to make relatively quick, noninvasive, in situ measurements (Weiner, 1984), this technique will be used in conjunction with the kinetic experiments to monitor particle formation and growth and to measure the diffusion coefficient (mass transport) parameter. The following discussion presents the theory of PCS in more detail, along with some applications in jet fuel thermal stress testing.

The optical setup of a PCS system is quite simple; a vertically polarized laser beam is focused into the sample of interest and a photomultiplier is used to collect the light scattered at some angle. The photomultiplier output signal I(t), the fluctuating intensity signal, is sent to a correlator, which performs an autocorrelation of the intensity fluctuation signal

$$G(\tau) = \langle I(t)\ I(t+\tau) \rangle,$$

where $I(t)$ and $I(t+\tau)$ are the intensity at times t and $t+\tau$, respectively. For a monodisperse suspension of particles

$$G(\tau)\ \alpha\ e^{-2\Gamma\tau},$$

where the exponential decay constant Γ can be expressed as

$$\Gamma = D\ q^2,$$

where D is the diffusion coefficient, and q the scattering wave vector

$$q = 4\pi n \sin(\theta/2)/\lambda_i,$$

with n the liquid refractive index, θ the scattering angle, and λ_i the incident laser wavelength. Particle size is determined using the Stokes-Einstein equation

$$D = k_B T/(3\pi\eta d),$$

where k_B is the Boltzmann constant, T the absolute temperature, η the fluid viscosity, and d the particle diameter.

To support the evaluation of the PCS technique, several commercial PCS devices have been used to measure particle sizes in thermally stressed JP-8 samples. These systems generally included a multi-angle measurement capability (important for polydisperse measurement accuracy), and a temperature-controlled test cell (Peltier heater, 20 to 80°C) to prevent convective flow from disturbing the measurements. The goals of these tests were to detect and correlate changes in particle size distributions with changes in the chemistry of the liquid and solid phase, as well as to determine applicability of a commercial PCS system to this program.

To provide sediment-containing samples, preliminary thermal stress tests were made by stressing fuel (JP-8 or JP-8X) in a 30 ml reactor made of 316 stainless steel, heated to the desired temperature by immersion in a sand bath. Fluid temperature, pressure, and exposure time were monitored. Desired temperatures were achieved in approximately 2 to 10 minutes, and the samples were allowed to cool to room temperature (about 3 minutes) prior to examination. Table 1 shows the test conditions and visual observations of fuel degradation for this series. Generally, the sample tested at the lower temperature was visually darker in color and exhibited similar or greater amounts of sediment than the sample tested at the higher temperature. Table 2 shows the results of PCS analysis of each of the

Table 1. Preliminary Thermal Stress Tests - Test Conditions

Fuel	T (°C)	P (psi)	Visual Observations
JP-8X	200	100 air	dark brown liquid, some sediment
JP-8X	250	100 air	yellow liquid, little sediment
JP-8X	201	330 air	dark brown liquid, much sediment
JP-8X	250	365 air	brown liquid, some sediment
JP-8X	200	300 N_2	light-yellow liquid, no sediment
JP-8X	250	300 N_2	light-yellow/clear liquid, no sediment
JP-8	300	300 air	light yellow liquid, no sediment
JP-8	350	300 air	light yellow liquid, no sediment

Table 2. Preliminary Thermal Stress Tests - Photon Correlation Spectroscopy Results

Fuel	T (°C)	P (psi)	Data Rate (kHz)	d (nm)	D (cm^2/s)
JP-8X	200	100 air	10-20	2500	5×10^{-9}
JP-8X	250	100 air	4-8	<3	n/c
JP-8X	201	330 air	n/m	2500	5×10^{-9}
JP-8X	250	365 air	20-30	3000	4×10^{-9}
JP-8X	200	300 N_2	1-1.6	<3	n/c
JP-8X	250	300 N_2	n/m	n/m	n/m
JP-8	300	300 air	30	3700	4×10^{-9}
JP-8	350	300 air	4	<3	n/c
JP-8	--	--	0.7	<3	n/c
Hexane	--	--	0.25	<3	n/c

n/m = not measured; n/c = no correlation detected stressed samples (after 10 micrometer filtering and dilution in hexane), along with two neat samples for comparison. The PCS device used in this analysis was a breadboard optical system combined with a Brookhaven Instruments BI-8000AT correlator. The temperature and pressure conditions under which the samples were stressed are provided, along with the data rate, the mean particle diameter (d), and the mean diffusion coefficient (D). The data rate listed in Table 2 is the mean intensity measured by the PCS system photomultiplier, a qualitative measure of the particle number density. The mean diameter is an intensity-weighted average of the distribution of different size particles detected. Note that for each sample pair, the sample exposed to a higher temperature has either comparable or fewer particles, with comparable or significantly smaller particle sizes. Examination of the JP-8X sample exposed to 250°C and 365 psi air with another PCS device (Coulter Model N4MD) gave similar results in that the mean particle size was fairly large (greater than about 3 micrometers). Static light scattering examination of this sample indicated that the particle size distribution was fairly monodisperse, in agreement with the PCS data.

Preliminary tests to determine the effect of exposure time to elevated temperature on particle formation were performed using a commercial PCS instrument, the Coulter Model N4MD. This instrument has a built-in multi-angle measurement capability and allows isothermal testing over the range 20 to 90°C by using a Peltier heater/cooler to maintain the test section temperature. Fuel samples were prepared as above, using a fluidized sand bath. Samples were heated to 185°C under 300 psi air for the desired exposure time. Exposure times of 10, 20, 30, 45, 60, and 90 minutes were used. The sand bath had a 6 to 7 minute heat-up time, and the stressed sample was cooled by a 3-minute quench. The PCS tests were performed 2 to 4 hours after heating. Samples were carefully transferred to a quartz cuvette and placed in the test chamber of the N4MD. Liquid properties used by the PCS software included the fuel absolute viscosity (μ=1.32 cP at 20°C, adjusted for higher temperature tests), and fuel refractive index (n = 1.37). Isothermal PCS tests were performed at 20, 40, 60, and 80°C test section temperature. The 45-minute sample was repeated 1 and 8 days later to examine the effect of time from stressing on the particle distribution. The pure, unstressed fuel gave essentially no counts on the PCS device, indicating a very low level of scattered light intensity detected by the photomultiplier and few particles of measurable size. The unstressed fuel count rate was 10^3 counts/s, while 10^5 to 10^6/s are needed for accurate PCS measurements. Figure 10 graphically displays the results of the exposure time tests; Table 3 lists the results. The general trend is toward larger mean diameter with increasing exposure time at fixed temperature. This finding is in qualitative agreement with visual observations of the color and presence of particles in the various stressed samples. The PCS technique has theoretical limitations on the size of the largest particles that can be measured with high precision (transition between translational and rotational diffusion). This limit appears to be on the order of several hundred nanometers, with particle sizes above this limit measurable but with lower precision. Therefore, the only reliable

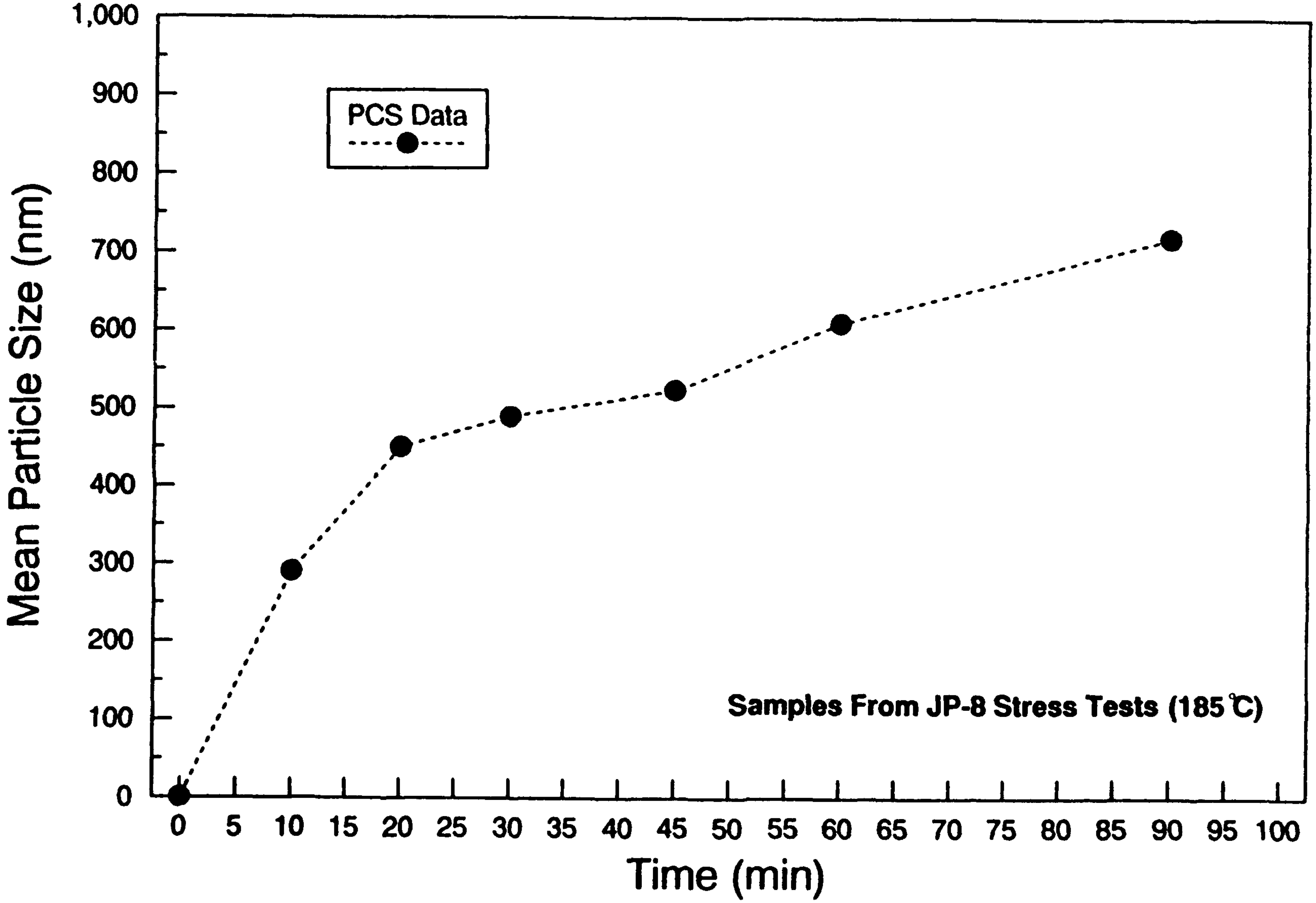

Figure 10. Mean Particle Diameter as a Function of Exposure Time.

Table 3. Mean Particle Sizes Measured in Thermally Stressed JP-8 Fuel Using PCS. All Samples Stressed at 185°C Under 300-psi Air.

Thermal Stress Time (min)	Mean Dia. (nm)	Standard Deviation (nm)
0	0	--
10	290	57
20	450	230
30	489	280
45	523	210
45^a	571	400
45^b	552	140
60	609	230
90	719	150

a = measurements one day after thermal stressing,
b = measurements 8 days after thermal stressing.

information that should be concluded from these data is that the particles tend to grow with increasing exposure time; a functional form of the growth curve cannot be inferred. Theory indicates that an exponential growth curve is typical for slow aggregation where the growth kinetics are reaction limited.

Figure 11 shows the measured scattered light intensity distribution data recorded during PCS tests. The intensity fractions are related to the relative number of particles in each size grouping. Figure 11 shows that increased thermal stress exposure time causes a shift of the distribution toward larger sizes. For these PCS measurements, essentially no particles less than 100 nm were detected; a small amount of particles with diameters greater than 1000 nm were detected in some of the samples, and only the

90-minute exposure sample appeared to have any particles with diameters above 2000 nm. The absence of large particles may be because of instrument limitations, insufficient exposure time or temperature to thermally stress the fuel, or because the particles settled from the liquid solution under the influence of gravity during the time between stressing and PCS testing. Assuming a minimum perceptible sedimentation velocity of 1 cm/h and spherical particles, calculation of the minimum diameter of particles that will settle under the influence of gravity yields a value of approximately 2000 nm (Sheludko, 1966). This may explain the absence of larger particles in the samples examined.

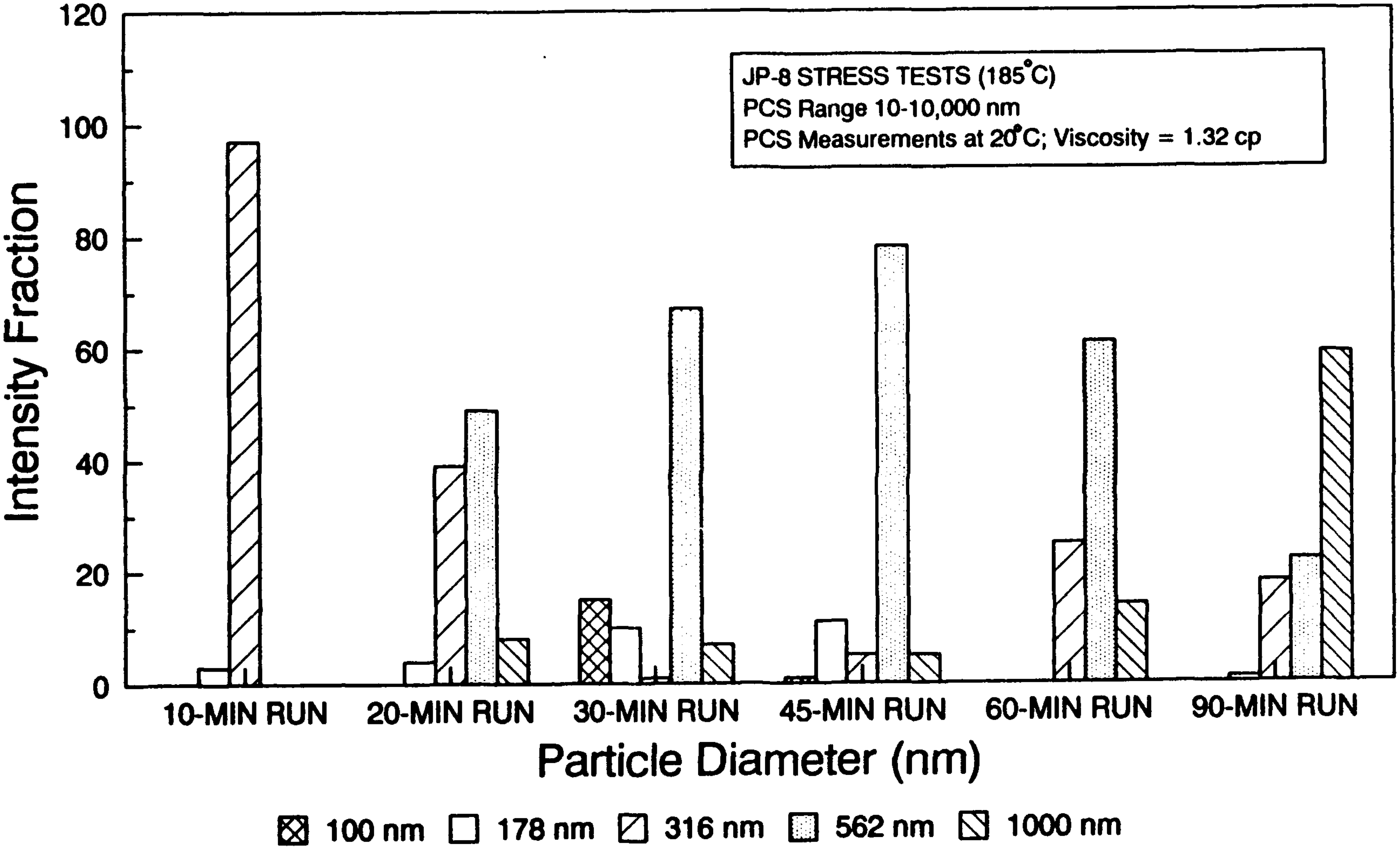

Figure 11. Particle Size Distributions as a Function of Exposure Time.

Figure 12 shows the effect of test section ambient temperature on mean particle diameter for a particular test sample (90-min exposure). Particle sizes were determined as the PCS sample temperature was increased, with measurements made at 20, 40, 60, and 80°C, and again at the same values as the temperature was decreased to 20°C. An equilibration time of 15 minutes was allowed, as recommended by the manufacturer. The measured particle diameters have been corrected for the change in fluid viscosity with temperature. The mean particle diameter decreased significantly with increasing test temperature, perhaps indicating a solubility effect. Not only did the mean diameter decrease, the particle size distribution indicated the presence of much smaller particles even at 40°C. Particles with diameters of a few tens of nanometers appeared, with particles of less than 10 nm detected at higher temperatures. With the exception of the measurements at 60°C, essentially no hysteresis was detected. The standard deviation of the particle diameters varied between 70 and 160 nm for all of these tests.

All of these results point out the need for true in situ measurements; they are needed for:

- assuring particle measurements are made at correct exposure time,
- elimination of particle settling effects, and
- assuring measurements are performed at test temperature.

Based on this need for in situ measurements, and the success of the PCS scoping tests, PCS has been chosen as primary technique for determination of particle formation. PCS appears to be the only technique able to perform the noninvasive measurements needed under the harsh test conditions. A PCS system has been designed, and the components ordered. The laser chosen for this system is a He-Ne, with 35-mW TEM_{00} output at 632.8 nm and 1000:1 vertical polarization. The unscattered portion of the illumination beam is collected by a power meter on the far side of the sample volume, allowing monitoring of laser power and extinction. The scattered light is collected with a low dark current Thorn EMI photomultiplier (Model 9863QB/100), whose output is amplified and discriminated by a Thorn EMI amplifier/discriminator (Model C604) to produce a uniform series of pulses with variable interpulse periods. This signal will then be sent to a Langley-Ford LFI 1096 digital correlator, where the autocorrelation is performed. This correlator has 256 real-time channels, and contains software allowing multi-tau data analysis;i.e., unequal time periods in the composition of the autocorrelation (for compatibility with existing software at SNL). The sample and the input laser beam have a fixed geometry, but the photomultiplier and amplifier/discriminator are mounted on an optical rail whose rotation about the sample cell is determined by a computer-controlled goniometer, allowing multi-angle measurements over a range from about 10 to 160 degrees off-forward. A Newport Model 855 controller and Model 496 rotary table

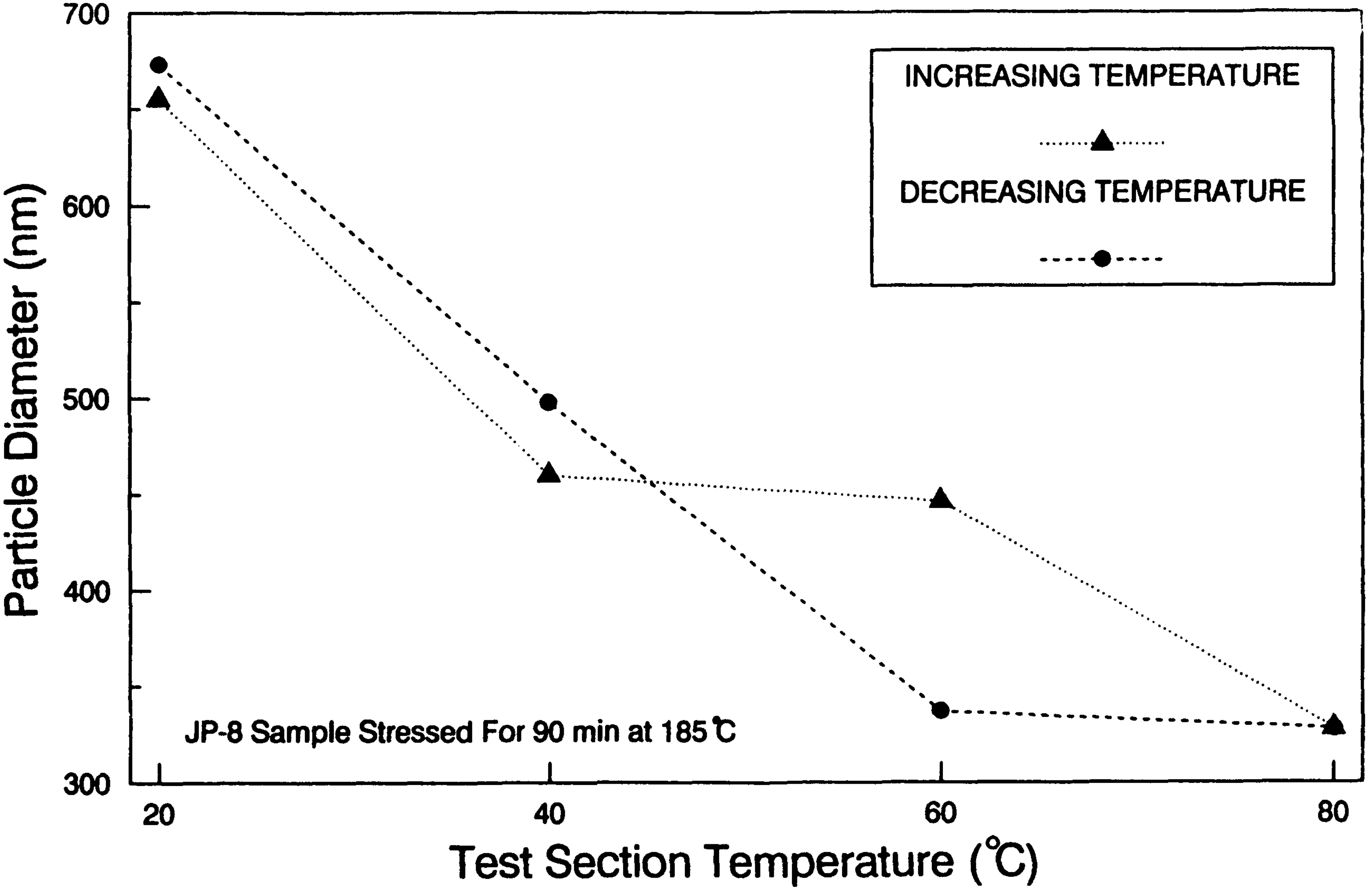

Figure 12. Effect of Test Section Temperature on PCS Measured Mean Particle Diameter.

comprise the goniometer. Additional lenses, apertures, and filters will be supplied from existing optical laboratory stock. A 386-based PC-type computer will be used for data acquisition and experiment control. Upon completion of the PCS system, it will be evaluated with known calibration particles for accuracy, precision, resolution, repeatability, and diameter range of applicability. The technique will be integrated with the Thermal Stress Cell for performing kinetic experiments. The data obtained will be used to determine diffusion coefficient distributions, to formulate models for particle growth, and for correlation with other chemical changes involved in the fuel degradation process.

Larger particle sizing in liquids (particle diameter greater than 1 μm) may also be needed. The results of the preliminary fuel thermal stress tests indicate that such large particles may be formed in thermal degradation of JP-8 and JP-8X (see above discussion), although the sizes may be an artifact of testing at ambient temperatures. Techniques for particle sizing in this range include sedimentation, laser diffraction, light scattering interferometry (phase Doppler), holography, and laser transit time analysis. As with the sub-micrometer measurements, sedimentation techniques are invasive, and require knowledge of the particle density. Laser diffraction instruments such as the Malvern or Coulter instruments record ensemble size distributions by measurement of the scattered light spatial distribution. Limitations on solution opacity, and unobstructed large aperture optical access, may limit the application of such systems to this program. The phase Doppler technique is probably not suitable for the present measurements because it requires spherical particles with a known refractive index. Holography records a three-dimensional image of all of the particles within a fairly large measurement volume (several liters or more), "freezing" their spatial locations for later analysis.

Diffraction limited resolution gives a minimum measurable particle diameter of about 1 micrometer, although optical noise usually pushes the achievable resolution up to several micrometers. The major drawback to the holographic technique is the tedious holographic reconstruction step needed for data reduction. The laser transit time analysis is a technique used in the Brinkmann particle sizing instrument, determining particle size by measuring the amount of time a particle obstructs a rapidly rotating laser beam. A built-in image collection and analysis system makes the Brinkmann instrument an attractive device for particle measurements in the 0.5 to 1200-micrometer-diameter range (system cost approximately $55K). If larger particle measurements are needed for this program, further evaluation will be made of holography and the Brinkmann device.

Measurement of Deposit Mass Accumulation

Real-time investigation of mass accumulation on surfaces during jet fuel degradation requires an extremely sensitive monitoring device. Because acoustic plate mode (APM) devices are capable of monitoring sub-monolayer mass accumulations at a solid-liquid interface, they are ideally suited for this application. As shown in Figure 13, these devices use interdigitated electrode patterns to excite and detect APMs on a piezoelectric quartz plate. Because the APM travels through the bulk of the piezoelectric quartz substrate with equal displacement at both surfaces, the unelectroded surface of the device can be used as the wetted surface for monitoring deposition. Mass accumulation rate as well as information about the viscoelastic nature of the deposit are determined by monitoring changes in the APM propagation characteristics, specifically the wave velocity and attenuation (i.e., loss of acoustic power).

To apply APM technology to the study of the thermal degradation of jet fuel, several modifications to the experimental apparatus were required. These included: (1) obtaining a sealant that can withstand contact with the heated jet fuel or redesigning the test case so that a sealant to the device is not required, (2) manufacturing a cell that allows the jet fuel to contact the device surface while preventing the vapors from escaping, and (3) establishing a procedure for safely heating the jet fuel under various atmospheres. With the experimental system in place, experiments to determine deposition rate as a function of time, temperature and atmosphere can be performed.

Two experimental configurations have been designed for this project. The first uses a high-temperature RTV silicone rubber sealant to seal the device into a metal flatpack used to make electrical connection to the device. The flatpack has a groove in the bottom that allows access to the unelectroded side of the device. In addition, a special Teflon cell, which seals to the flatpack containing the APM device, has been designed. This cell maintains the jet fuel in contact with the sensing surface. A reflux condenser is seated in the top of the cell to condense vapors produced during an experiment. This prevents loss of the liquid and greatly decreases the vapor pressure of flammable species in the atmosphere outside of the test fixture. This test fixture has been fabricated and satisfactorily tested using jet fuels at room temperature and model jet fuels (styrene in dodecane) at elevated temperature (up to 130°C). The second modification is to have a probe card (a PC board with specially placed pins for making electrical contact) designed and fabricated for use with the APM devices. In this arrangement, the Teflon cell is used to press the device to the probe card, allowing simultaneous electrical contact to the device and a seal directly to the quartz substrate. This configuration removes the need for silicone rubber or other compliant elastomer to form a liquid tight seal. The test case to hold the device has been designed and fabricated. The probe cards have been designed and are currently being manufactured and fitted to the test case. This test system has the advantage of simpler and more durable sealing along with easier exchange of devices.

Two techniques for heating the liquid have been tried to date. The first utilized a hot plate to heat the case containing the liquid and device from below. Using this technique, the temperature of the liquid could not be raised above 80°C without excessive heating of the case (hot plate surface

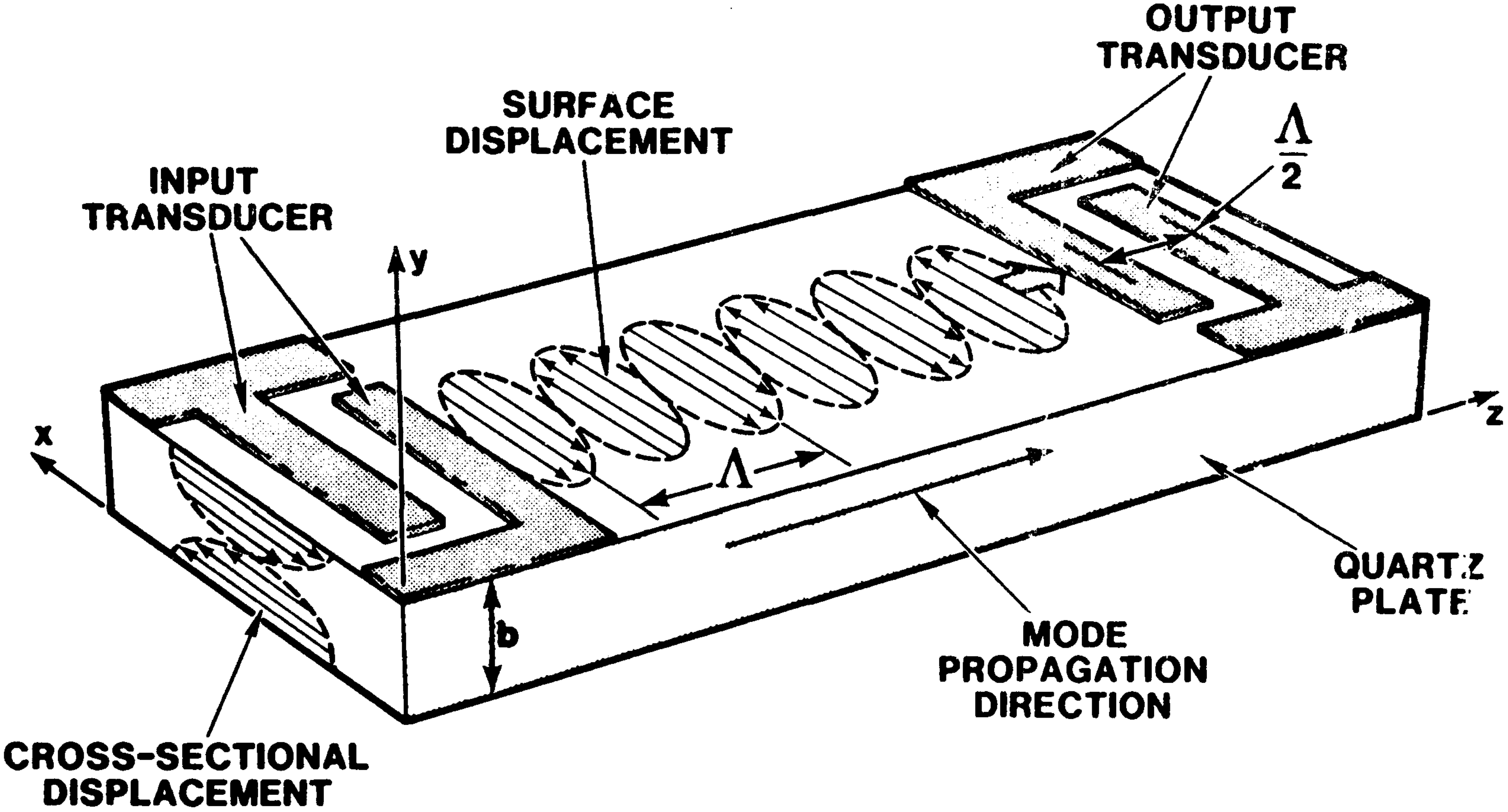

Figure 13. Schematic of Acoustic Plate Mode Device.

temperature greater than 200°C). Rather than making the alterations necessary for maintaining electrical contact at these higher temperatures, heating mechanisms that provide more directed heating of the liquid and device were investigated. The second experiment utilized a resistive heater immersed in the liquid to heat the liquid and device. Based upon an immersed thermocouple, liquid temperatures near the device of 130°C were achieved. A deposition experiment was performed with this configuration. After heating 2 ml of dodecane to 130°C, 0.1 ml of styrene was added to simulate conditions in which surface deposition occurs. A transient response was observed due to temperature fluctuations of the mixture upon addition of the room temperature styrene. Based upon the relatively small frequency shift obtained by comparing the signal before and after this transient, minimal surface deposition was detected. By placing the thermocouple at various locations in the liquid, it was determined that the device temperature was significantly lower than the liquid temperature near the heater. Consequently, the majority of the deposition of styrene is postulated to have occurred on the resistive heater rather than on the device surface. The next set of experiments will be directed toward more uniform heating of the liquid and device using an oven.

Experiments were also performed using pre-stressed jet fuel to evaluate the capabilities of APM devices to monitor deposition. These experiments used jet fuel that had been thermally stressed in air at 200°C and 300 psi. After cooling, the jet fuel was placed in the cell and the device frequency (used to monitor changes in the wave velocity and linearly proportional to the change in mass accumulation) and insertion loss (directly related to wave attenuation and the viscoelastic properties of the material) were monitored with time. The results are shown in Figure 14. A steady and significant frequency decrease was observed which continued throughout this 5-hour experiment. If it is assumed that this frequency change is mainly due to mass loading of the device, the rate of frequency change can be used to calculate the deposition rate using calibration values obtained by monitoring frequency changes during vacuum evaporation of metals onto the device surface. For this run, the slope of the frequency curve of -20.6 ppm/h translates into a deposition rate of 1100 ng/cm^2/h. This is the order of magnitude of deposition rate that might be expected in flow experiments (see e.g., Vranos et al., 1981; Taylor and Wallace, 1967). If the density of the deposited layer is assumed to be 1.0 g/cm^3, a deposition rate of 1.1 μm/h is predicted. A second experiment was performed using the same thermally stressed jet fuel after filtering through a 0.45-μm filter. The frequency and insertion loss changes with time are shown in Figure 15. The frequency initially increases slowly, probably due to temperature changes occurring as the liquid, device and the test case become temperature equilibrated. After approximately 2 hours, the frequency starts to decrease at a relatively constant rate indicating an increase in mass on the surface during deposition. The slope of the frequency curve of -8.23 ppm/h translates into a deposition rate of 430 ng/cm^2/h or 0.43 μm/h if the density is again assumed to be 1.0 g/cm^3. This is about a factor of 3 slower than the unfiltered case. In both experiments, the insertion loss increases as the deposition occurs. This indicates that the deposited

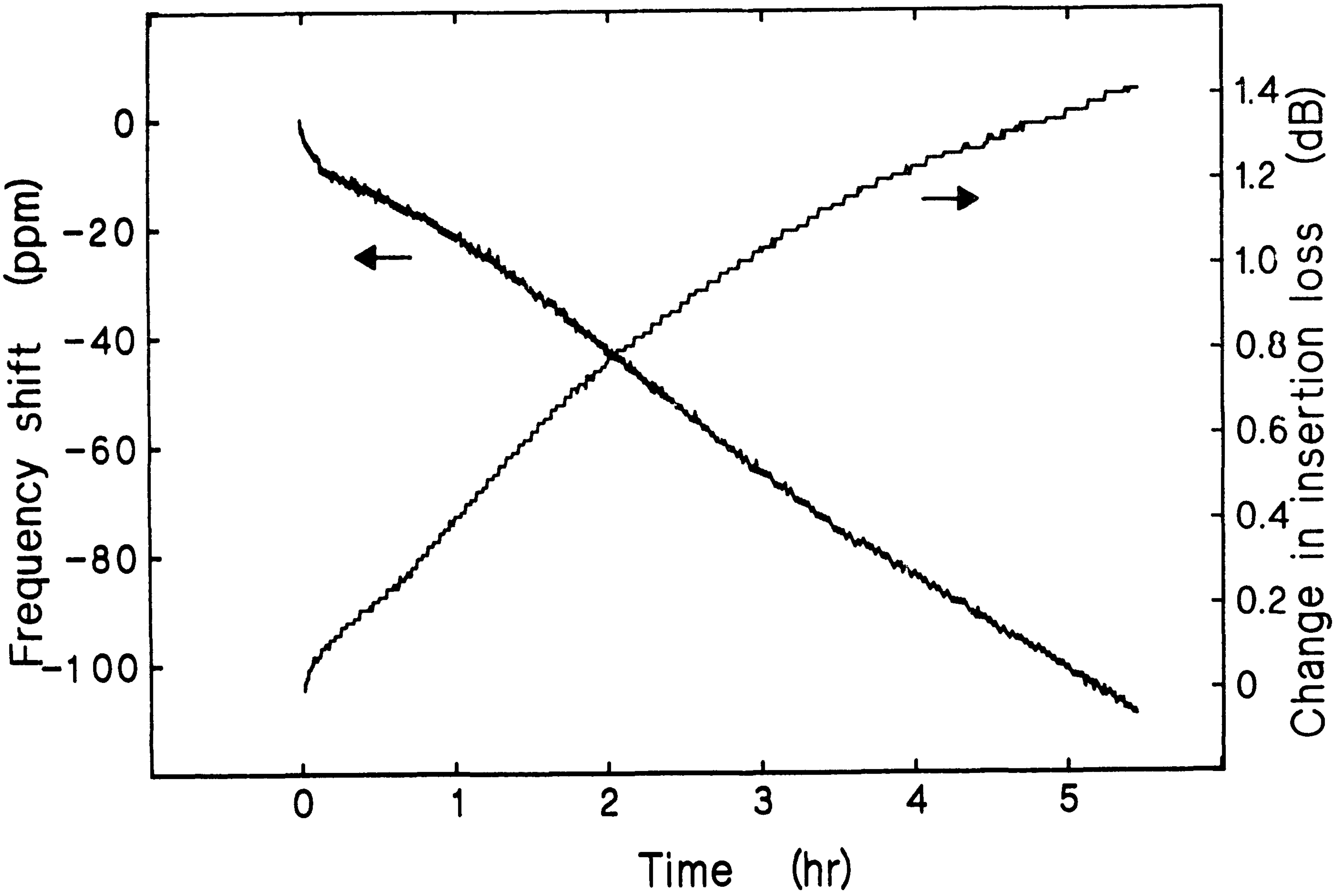

Figure 14. APM Frequency Shift and Insertion Loss for Unfiltered, Thermally-Stressed JP-8 Fuel.

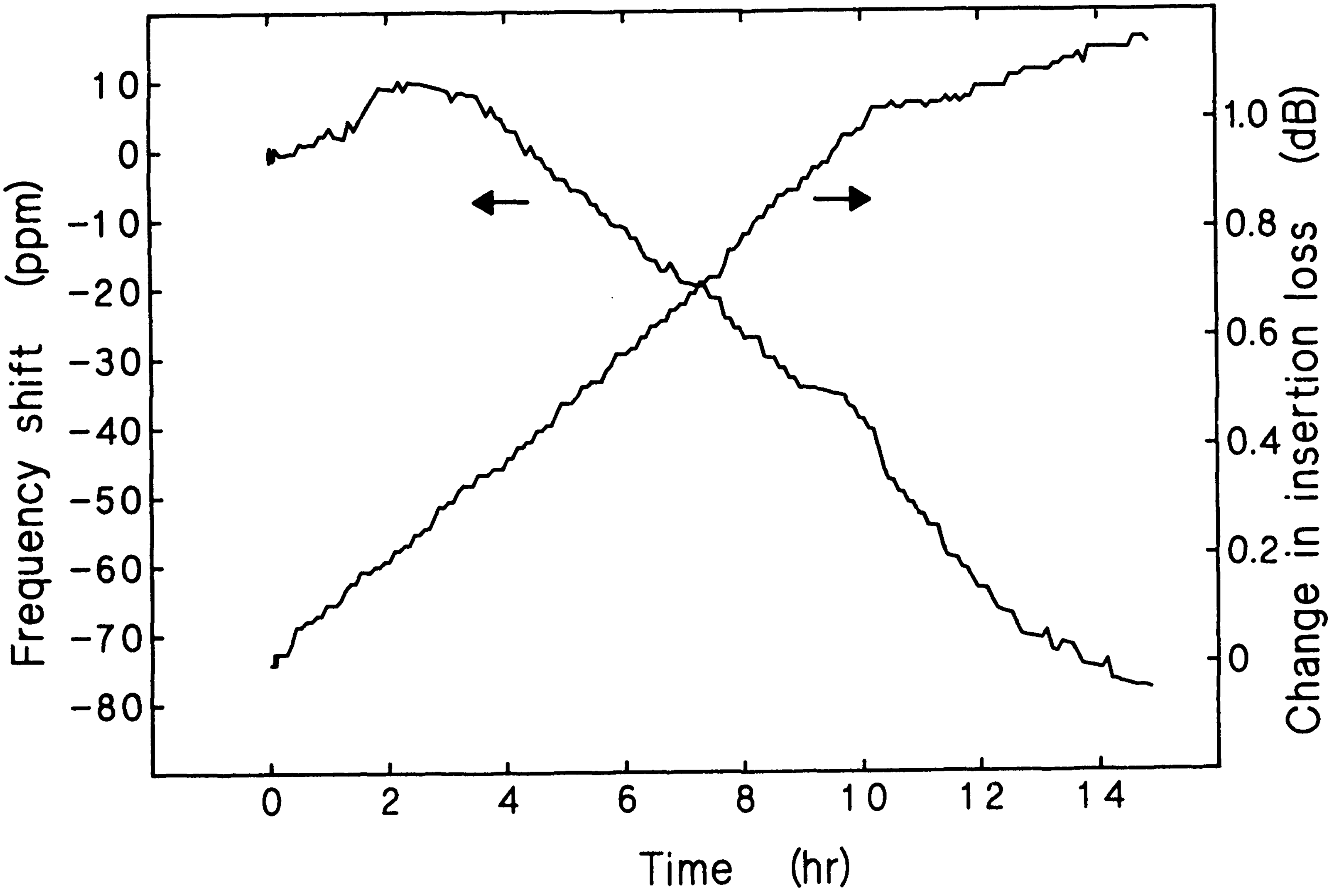

Figure 15. APM Frequency Shift and Insertion Loss for Filtered, Thermally-Stressed JP-8 Fuel.

layer is relatively soft, resulting in attenuation of the wave due to the viscoelastic nature of the deposit. Using a model for the film/APM interactions, it should be possible to use the relative magnitudes of the frequency and insertion loss responses to provide information about the viscoelastic properties. The fact that the insertion loss appears to level out with time while the frequency response continues to decrease may indicate that the deposit is stiffening with time.

Future work will focus on performing experiments to monitor deposition at elevated temperatures. Experiments to probe the effect of atmosphere (i.e., oxygen content) as well as the nature of the surface (i.e., quartz, copper or nickel) on deposition rate will be performed. Work to integrate an APM device into the Thermal Stress Cell will be performed allowing the deposition rate to be monitored in future kinetic experiments.

Sediment and Deposit Characterization Techniques

Samples of solid deposits were obtained from the Aero Propulsion Laboratory, Wright-Patterson Air Force Base, in the form of post-test tubes run on the Jet Fuel Thermal Oxidation Tester (JFTOT). Solid deposits were also produced for analyses by thermally stressing jet fuel samples provided by WPAFB. A broad array of analytical techniques can be considered for analysis of insoluble deposits. In particular, characterization of the deposit thickness, chemical composition, and type of bonding are desired. The major driving force that narrows the array of analytical techniques is that the primary species are relatively light elements, i.e., carbon, oxygen, hydrogen and nitrogen; along with perhaps trace amounts of metal impurities. Second, the thickness of the deposits that must be examined are often on the order of micrometers and may be less than this amount. These considerations rule out the use of several analytical techniques and drive the investigator in the direction of either surface analytical techniques or optical techniques. The following techniques have been identified as potentially useful for characterizing these deposits:

- Secondary ion mass spectroscopy (SIMS) and sputter depth profiling
  - good surface sensitivity and light element detection;
  - some molecular bonding information obtained.

- Auger electron spectroscopy (AES) and sputter depth profiling
  - good surface sensitivity and detection of elements $Z \geq 3$ (Li);
  - relatively high threshold concentrations compared to SIMS.

- Fourier transform infrared (FTIR) spectroscopy
  - permits identification of organics and some inorganics;
  - high sensitivity for light impurities;
  - generally better than Raman spectroscopy for organic molecules.

- Energy dispersive x-ray fluorescence
  - ability to identify trace metallic impurities;
  - generally limited to elements $Z \geq 11$ (Na).

- Laser desorption/ionization Fourier transform mass spectrometry (LDFTMS)
  - information on solids structure and composition;
  - high mass resolution allows identification of organic and inorganic ions;
  - can fragment ions to study possible formation process.

Secondary ion mass spectroscopy (SIMS), Auger electron spectroscopy (AES) and x-ray fluorescence are being used to determine the elemental composition of deposits as a function of position on the aluminum test tubes. Ion-beam sputtering coupled with SIMS and AES is being used to determine thickness of deposits as a function of position. Fourier Transform Infrared Spectroscopy (FTIR) is being used to aid in identifying the type of bonding present in the JFTOT deposits. LDFTMS is being used to identify compounds and ions present in the solids deposit and study possible mechanisms of solid deposit formation.

SIMS, Auger Electron Spectroscopy, and Ion-Beam Depth Profiling Studies

Ion-beam depth profiling was applied to determine deposit thickness as a function of position on the axis of a tube (referred to as tube H) used in a JFTOT test. Xenon ions were accelerated to 5 keV and used to sputter at a given position along the tube axis. The SIMS oxygen peak was monitored in order to determine when the deposit had been sputtered through, and the Al_2O_3 on the surface of the aluminum tube had been reached. The results of the ion beam sputtering experiments on the tube (produced from a JFTOT test using JP-8X fuel) are shown in Figure 16. Results of the TDR (Tube Deposit Rater) profile obtained during the JFTOT specification test, as described by ASTM D3241, are also shown on the figure (the maximum value of the relative thickness was arbitrarily set equal between the two methods to facilitate comparisons). When the thickness profile obtained by the quantitative ion beam sputtering analyses is compared to the TDR profile, qualitative but not quantitative agreement is noted. This difference is undoubtedly due to situations by which the TDR values are disproportionately influenced by thin, highly colored deposits. This susceptibility limits the usefulness of the TDR as a tool for quantitative measurements. Studies have been initiated to prepare photoresist standards in order to obtain absolute thickness measurements of the deposits. Preliminary results indicate that the maximum thickness shown in Figure 16 is on the order of 1.5-2 micrometers.

AES and SIMS have been used to determine the elemental composition of the tubes. Figure 17 is an Auger spectrum from a typical tube. These data indicate that the deposit is primarily carbon (Auger does not detect hydrogen) with small quantities of S, N, and O. SIMS data from the same tube indicate the presence of hydrogen and small quantities of Na, Mg, Al, Si, K, Ca, Fe, and Cu in addition to the S, N, O, and C observed in the Auger spectrum. The choice of which technique to use to analyze the tubes depends on the desired information. SIMS can be used to detect trace quantities of a wide variety of elements. It is difficult to quantify, however. Auger has a detection limit of about 0.5 percent but is much

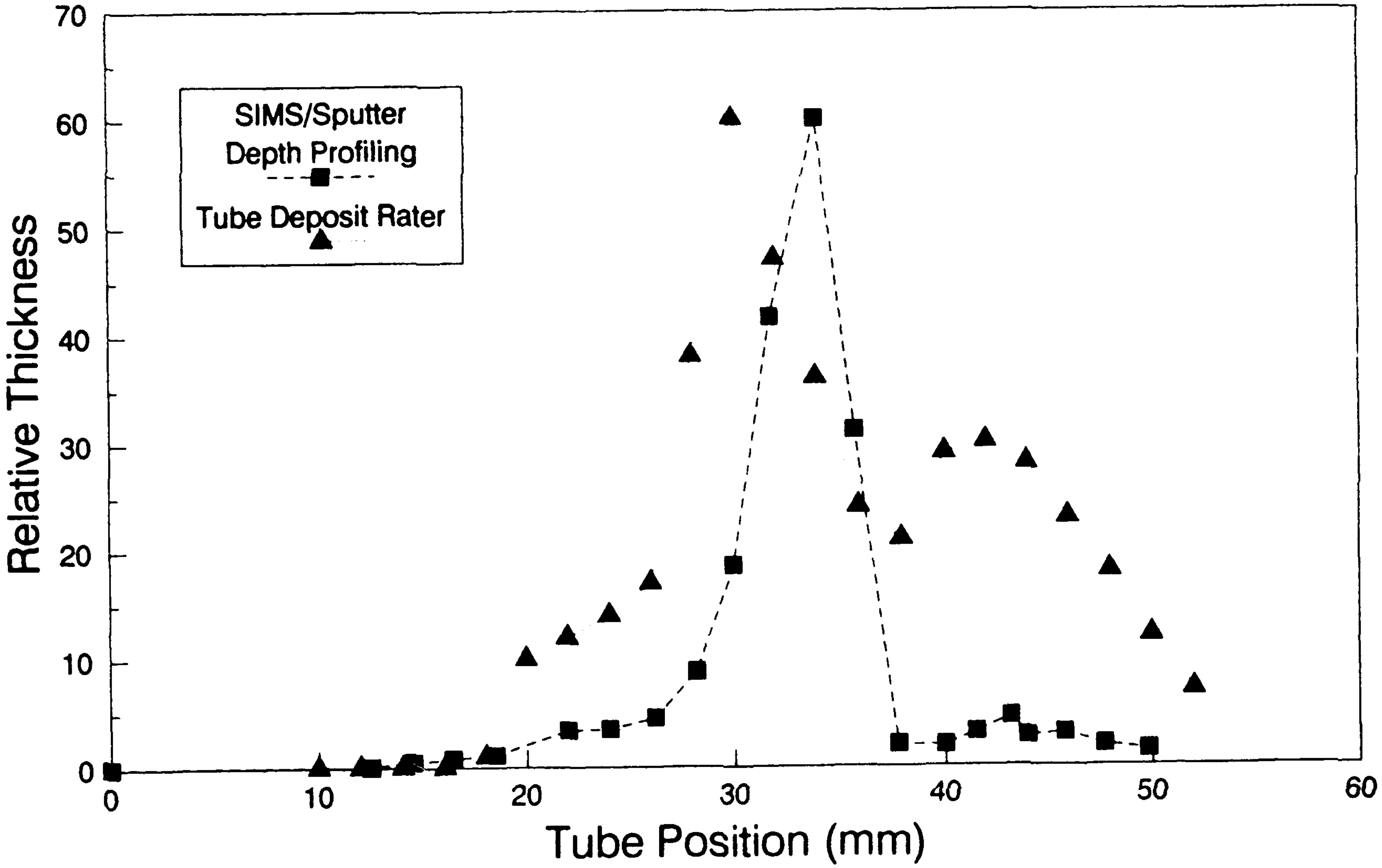

Figure 16. Comparison of Depth Profile on JFTOT Tube H Using SIMS/Sputter Depth Profiling and Tube Deposit Rater.

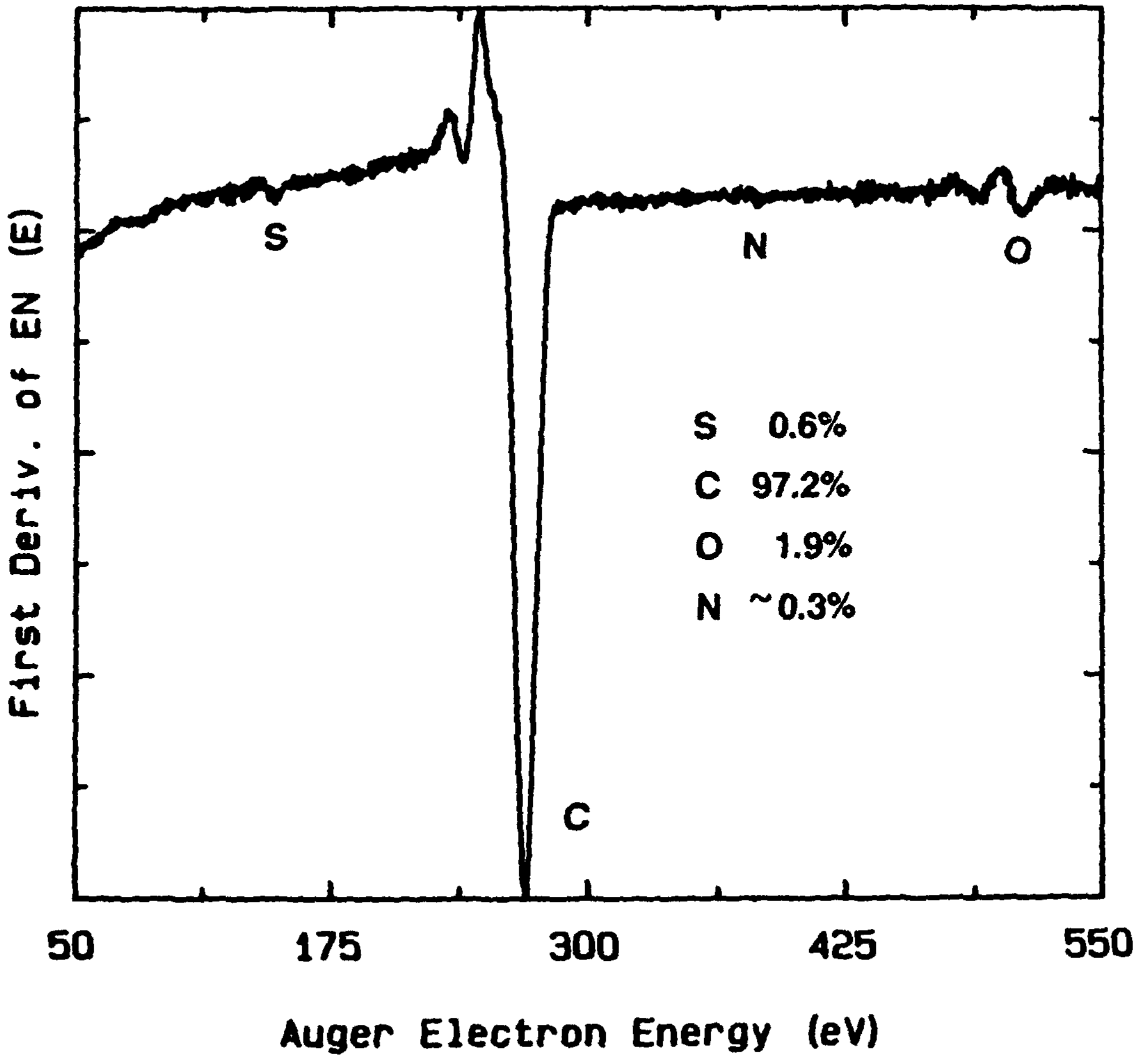

Figure 17. Typical Auger Spectrum From Tube H.

easier to quantify. It appears S, O, and N are usually present in sufficient quantities to be detected by Auger and if these are the elements that are most important, Auger may be the technique of choice. Either Auger or SIMS can be combined with ion beam sputtering to determine the thickness of the deposit.

SIMS spectra and depth profiles were obtained using a rastered 5 keV Xe^+ ion beam. While obtaining the SIMS spectra the ion beam was rastered over a 1- by 1-mm area and all of the signal was accepted in the analyzer. For the depth profiles the beam was rastered over a 1- by 1-mm area and only the signal from the center 0.3- by 0.3-mm area was accepted in the analyzer. Both the oxygen and carbon signals were monitored during depth profiling. Depth profiling was performed at approximately 2-mm intervals along the deposit section length of JFTOT tube H.

The depth profile from JFTOT tube H, which has the thickest deposit layer, is shown in Figure 18. The carbon and oxygen intensities were monitored as a function of sputter time. The oxygen signal is high at the surface and then drops to near zero until the deposit-aluminum interface is reached. At this point the oxygen signal rises and again drops as the oxide layer on the aluminum is penetrated. The time to reach the peak of the oxide layer was used as a relative measure of the thickness of the deposit. The sputter time will be calibrated using appropriate thickness standards, which are being prepared.

The surface spectra from the area of tube H with the thickest deposit are shown in Figures 19 and 20. The negative ion spectrum, Figure 19, shows peaks due to H, C, O and Cl (may be a sulfide ion) as well as molecular combinations of the first three elements. For example, prominent peaks due to C, CH_2, C_2, C_2H and C_2H_2 are seen. The positive ion spectrum, Figure 20, shows, in addition to CH_x molecules the elements Na, Mg, Al, Si, K and Ca. SIMS has very high sensitivity for Na, K, and Ca, and these common contaminants are seen in most samples. However, all of the molecular species that are present in the spectra are consistent with expected components of the solid deposits. Sulfur was not identified at mass/charge ratio of 32 in the SIMS spectra even though we had previously observed a small amount in the Auger electron spectra. This may be due to a molecular interference with O_2, which also falls at mass/charge ratio of 32.

The use of SIMS in combination with ion-beam depth profiling appears to be extremely useful for obtaining a qualitative chemical information on elemental and simple molecular species which are present in fuel deposits. The technique also has promising potential for use as an alternative to the reflectance technique in the JFTOT test for measurement of deposit thickness--especially if the tubes can be run in the instrument immediately after JFTOT testing.

Fourier Transform Infrared (FTIR) Spectroscopy Studies

JFTOT tubes were examined using the Nicolet 7199 FT-IR spectrometer with a

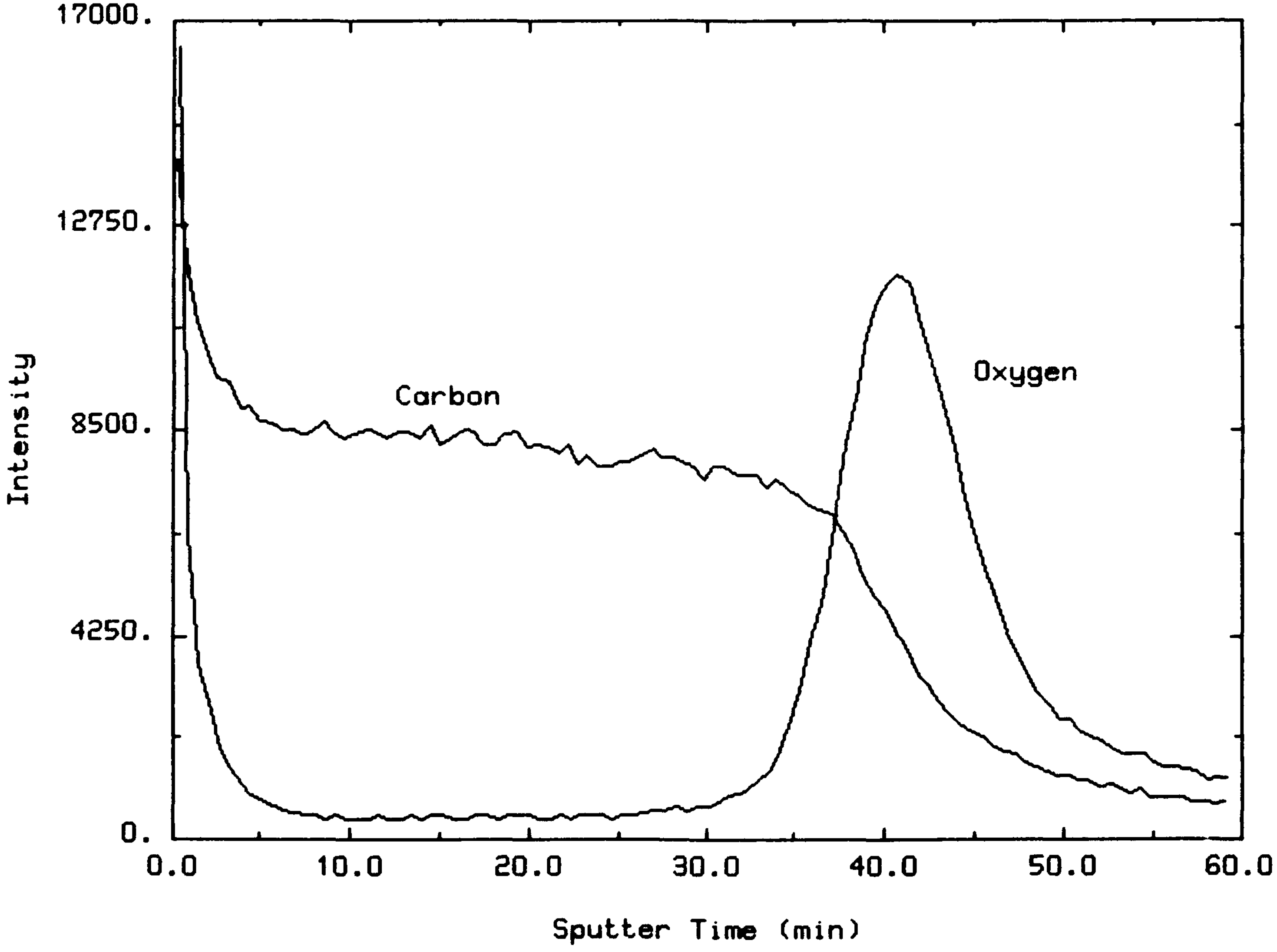

Figure 18. SIMS/Ion Beam Depth Profiling Results for JFTOT Tube H.

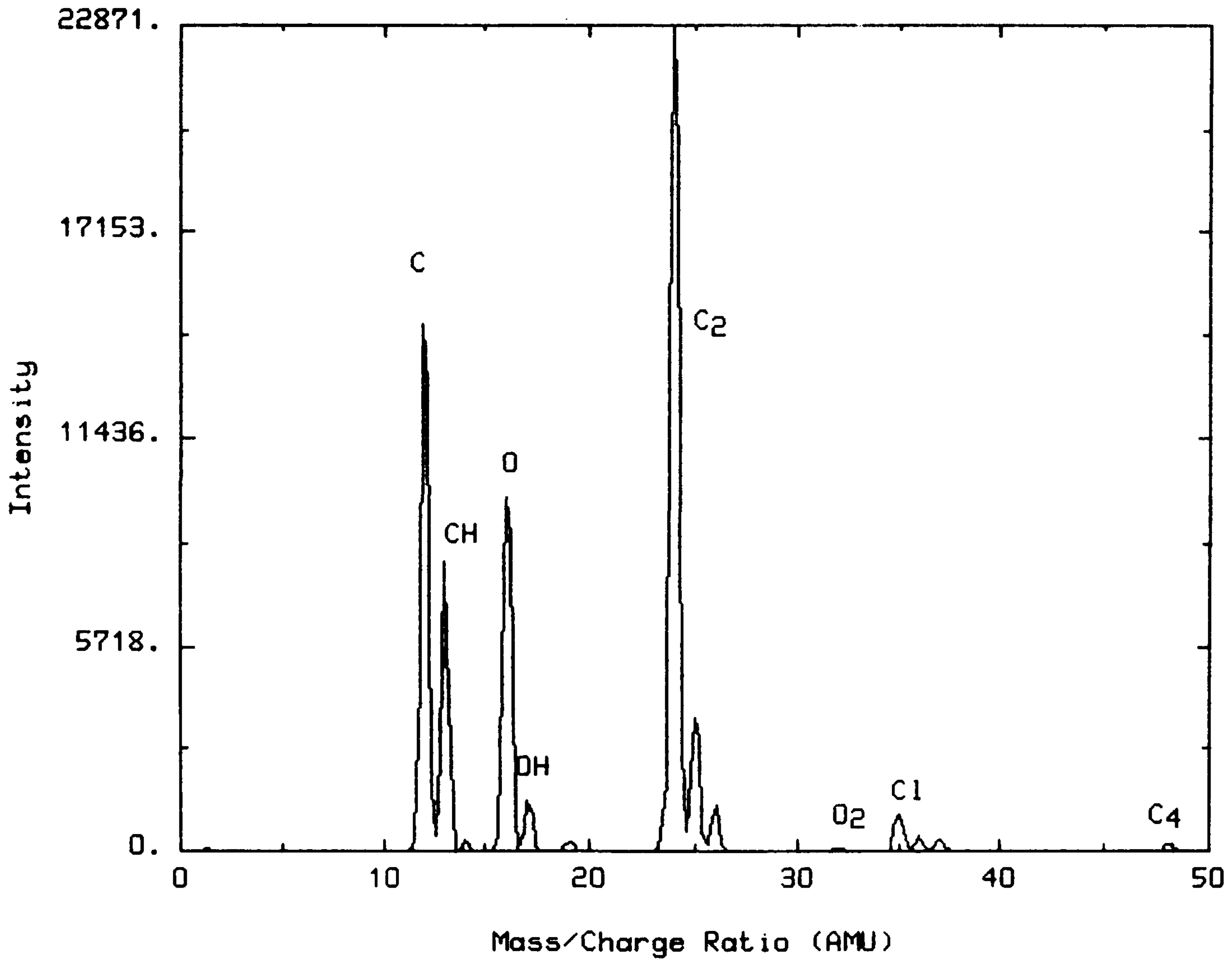

Figure 19. SIMS Negative Ion Spectra for the Surface of JFTOT Tube H.

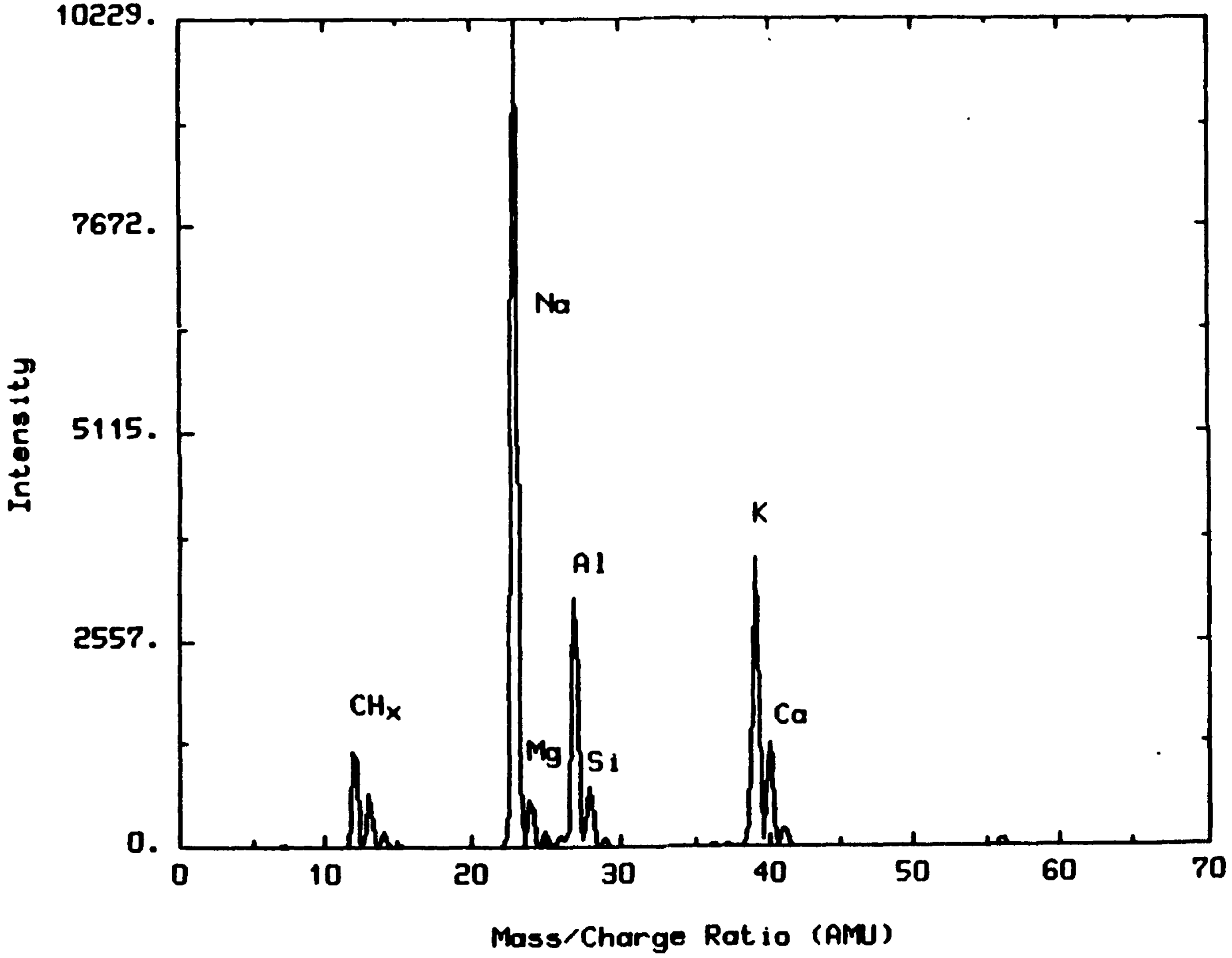

Figure 20. SIMS Positive Ion Spectra for the Surface of JFTOT Tube H.

microscope accessory in reflection mode. Tubes A and B involved the use of JP-8 while tubes C and D were generated using 11.4 mg/L JFA-5 added to the JP-8 fuel. The IR spectrum from tube A contained primarily a carbonate deposit with a slight amount of an unidentified hydrocarbon. Tube B was coated with a deposit that appeared to be a copolymer such as poly(ester/propylene). The spectra from tubes C and D did not contain adequate signal-to noise ratios to make an identification of the deposits. Characteristic of the deposits on tubes A and B was the presence of oxygenated carbon species. This technique appears to be useful in identifying organic compounds and functional groups present in solid deposits. Its ability to quantify concentrations in the solids suggests that it can be successfully used in conjunction with another technique such as LDFTMS to determine and quantify the organic compounds present in the deposits.

Energy Dispersive X-Ray Fluorescence Studies

Energy dispersive X-ray fluorescence spectroscopy was used to analyze tubes A, B, C, and D. A baseline spectrum was acquired using the end of a tube not exposed to the sample chamber. The baseline Al tube is far from pure, containing the following elements in a rough order ranking: Al, Cu, Fe, Mn, Zn, Cr, Zr, Sc, Ti, Ni, Ga, and Ca. The only element present in the deposits that is not present in the baseline material is S. Qualitatively, tube B (which visually had the darkest deposit) was found to have the largest amount of sulfur, with C & D having slightly less, and A (whose film was almost visually absent) showed the least amount of sulfur. Note that Na is the lightest element on the periodic table that is detectable by this technique. The presence of S in these tubes is consistent with the Auger and SIMS data from tube H. This technique is useful in determining trace amounts of metals that might catalyze deposit formation and reaction.

Preliminary Examination of Jet Fuel Particulates Using Laser Desorption Fourier Transform Mass Spectrometry (LDFTMS)

Laser desorption/ionization Fourier transform mass spectrometry (LDFTMS) is a technique that is being evaluated to investigate the composition and structure of the solid deposits. Fourier transform mass spectrometry is a relatively new form of mass spectrometry that capitalizes on the relationship between an ion's cyclotron resonance frequency in a magnetic field and its mass to charge ratio (m/z). The technique is characterized by high mass resolution and the ability to trap and observe ions for extended periods of time, facilitating experiments in gas phase chemistry (Buchanan, 1987). One particularly useful FTMS technique consists of isolating an ion of interest followed by fragmentation to study the ion's formulation (MS/MS). The incorporation of laser vaporization/ionization with FTMS is commonly used in experiments with solid samples that would be difficult to vaporize by more conventional techniques.

Samples of jet fuel were heated under 300 psi air at 220°C for 1 hour. This treatment caused a darkening of the fuel, and the formation of numerous particles of solid material that precipitated upon standing. The particles were allowed to settle onto 0.5 mm thick by 25.6 mm diameter stainless steel discs; after coverage was complete, the discs were removed and dried under a heat lamp to remove excess jet fuel. The discs were then mounted on the laser sample holder assembly in preparation for insertion into the FTMS 2000 vacuum chamber. The sample holder assembly with the sample discs was placed on the FTMS direct insertion probe and inserted into the vacuum chamber to the point where a CO_2 laser is focussed on the disc. The laser power was adjusted so that a strike on a carbon beam block was barely visible. The probe can be rotated in a step- wise fashion so that 72 laser shots are obtainable from a single sample disc.

The formation of both positive and negative ions from the precipitated solids following laser vaporization has been investigated. Negative ion spectra were characterized by the formation of small carbon clusters containing from 5 to 14 carbon atoms with a maximum intensity at C_8. See Figure 21. These clusters are very similar to the negatively charged carbon clusters achieved from graphite by Knight et al. (1986) using a Nd:Yag laser in conjunction with FTMS.

Very few positive ions were formed on the "as precipitated" laser discs. Since other workers have achieved enhanced ionization from laser desorption by coating samples with salts of alkali metals (Hardin et al., 1984), a few drops of methyl alcohol solution saturated with potassium bromide were added to laser discs coated with the jet fuel particulate material. Figure 22 is a positive ion mass spectrum obtained following this treatment. Note in the figure inset that the peak shown at mass 32 u can be resolved into two isobaric peaks. Table 4 compares the measured masses from the spectrum in Figure 22 to calculated masses for a number of elements and molecules or molecular fragments in the mass range of interest. The ion shown with the

Table 4. A Comparison of FTMS Measured Masses From Jet Fuel Particulates to Calculated Masses.

Ion	Calculated Mass (u)	Measured Mass (u)	Diff. (u)	% Diff.
H_3O	19.0184	19.0295	0.0011	0.006
^{23}Na	22.9898	22.9914	0.0016	0.007
C_2H_2	26.0157	26.0176	0.0019	0.007
^{28}Si	27.9769	27.9793	0.0024	0.009
^{29}Si	28.9765	28.9789	0.0024	0.008
^{30}Si	29.9738	29.9750	0.0012	0.004
^{32}S	31.9721	31.9749	0.0028	0.009
O_2	31.9898	31.9927	0.0029	0.009
^{34}S	33.9679	33.9711	0.0032	0.009
^{39}K	38.9637	38.9666	0.0029	0.007
HCO_2	44.9976	44.9848	-0.0078	-0.017
HCS	44.9799	44.9848	-0.0049	-0.011
^{44}Sc	44.9559	44.9848	0.034	0.075

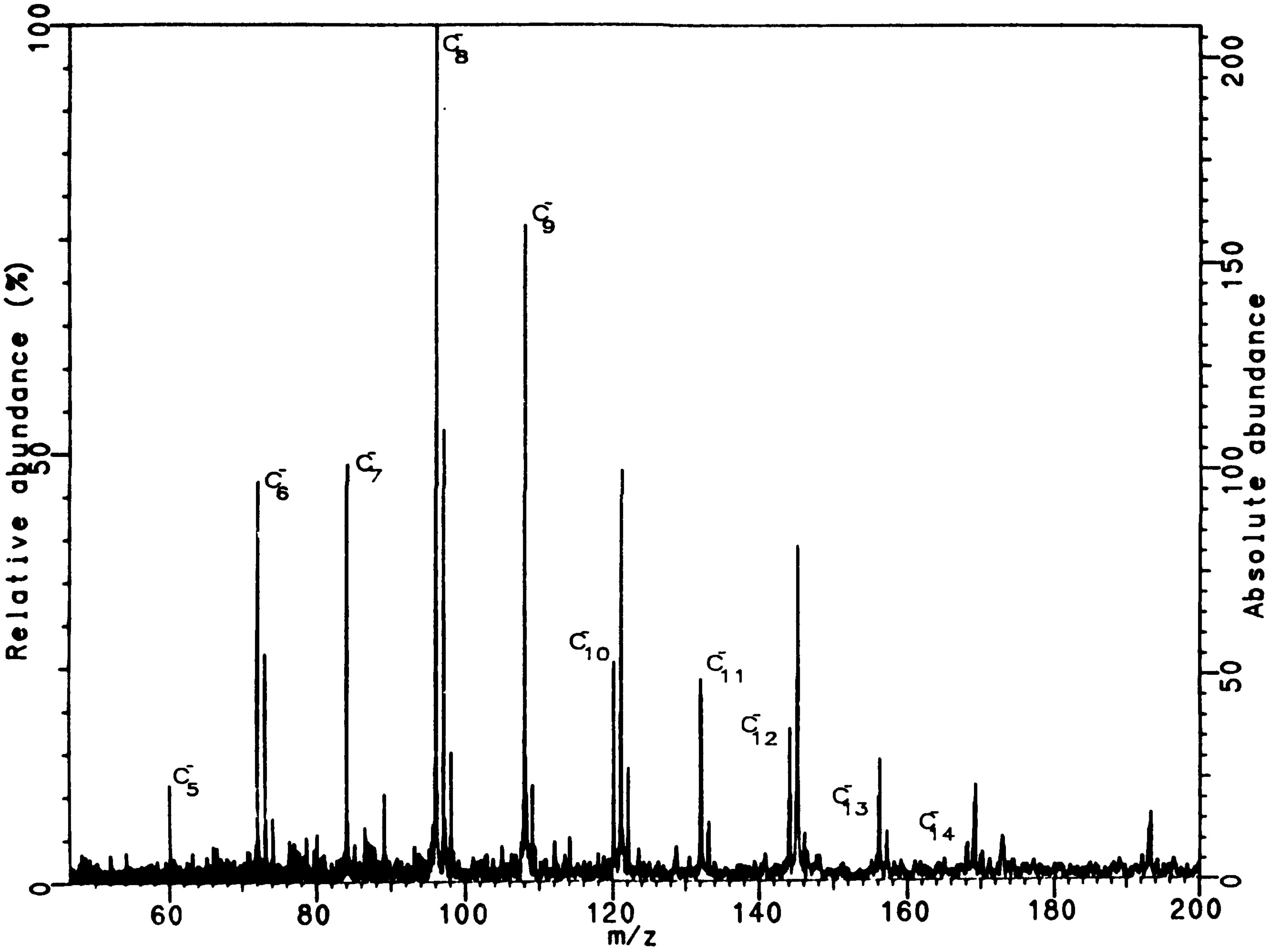

Figure 21. Negatively charged carbon clusters Cn where 4<n<15.

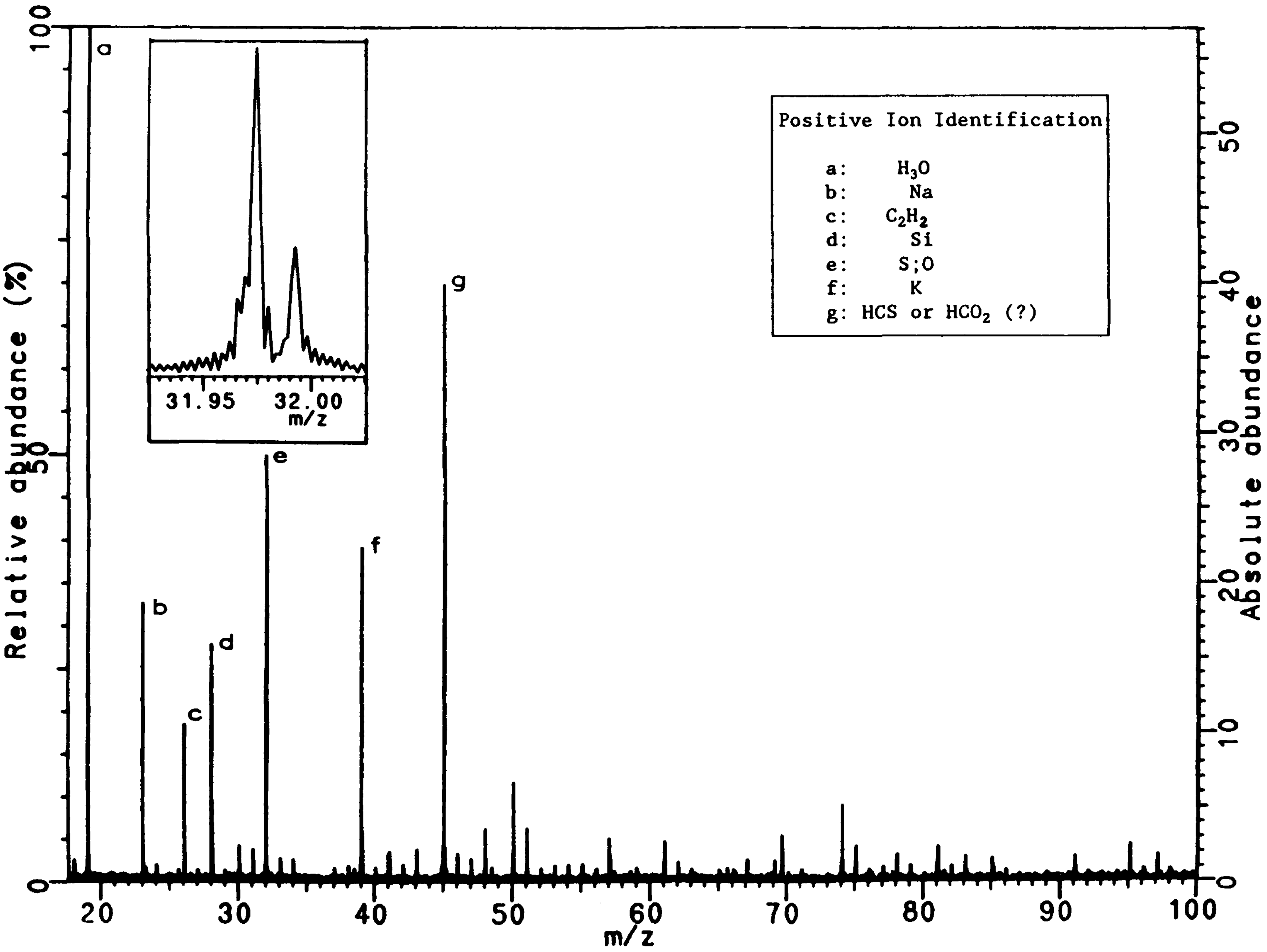

Figure 22. Positive Ion Mass Spectrum for the Low Mass Ions.

highest intensity in Figure 22 is that of the hydronium ion (H_3O^+). The presence of this ion is explained by an abundance of occluded water, which is easily protonated by ion/molecule reactions with either itself, or hydrocarbons. The long delay times between ionization and ion detection required for laser desorption mass spectrometry favors this reaction. The presence of sodium in the spectrum is possibly a contaminant added with the KBr. Although difficult to see in Figure 22, the presence of ^{29}Si and ^{30}Si isotopes in the proper abundance ratios to ^{28}Si confirm the presence of silicon in the samples. Sulfur is confirmed by the proper intensity of the ^{34}S isotope, and on magnification (see figure inset), O_2 can be easily resolved from ^{32}S. Table 4 lists three possible identifications for the ion at mass 45, however, none of these entities have the same mass accuracy achieved for the positively identified elements or fragments.

As would be expected from a sample collected in the manner described above, ion intensities vary considerably in mass spectra collected from various spots on the discs. However, ion abundance trends were observed when multiple laser shots were made on the same spot. Generally only potassium ions were observable following the first laser strike on a given spot. The second and third strikes show increases in the intensities of the ions that appear in Figure 22. Following these strikes, there is also the advent of the mass spectral fragment pattern shown as Figure 23. After the third laser shot on the same spot, most of the low mass ions disappeared, and there was the appearance of two peaks at masses 213 and 215, a group of four peaks at masses 275, 277, 279, and 281 (determined to be $K_3Br_2^+$ formed from the sample dopant), and carbon clusters containing 50 ($m/z = 600$) and 60 ($m/z = 720$) carbon atoms. See Figure 24.

Figure 23 is similar to the mass spectra of polyunsaturated or cyclic oxygen compounds (alcohols, ethers, or aldehydes). These compounds are expected products of fuel degradation. It is obviously the spectrum of a mixture of materials; however, it has many of the same features as a library mass spectrum of the cyclic aldehyde longifolenaldehyde.

The peaks that appear at masses 213 and 215 have not been positively identified. Mass measurements and the ratio of the two peaks suggest that this grouping is due to an ion containing five or six sulfur atoms. Gas-phase polysulfides with formulations of FeS_n^+ ($n = 1\text{-}6$) have been recently reported (MacMahon et al., 1989); however, neither iron nor any of the other transition metals with a formulation of MS_5 or MS_6 have a mass of 213. Further experiments to determine the formulation of this species using MS/MS techniques are planned.

Stable, positively charged carbon clusters containing 40 to 80 carbon atoms have been formed from graphite (Kroto et al., 1985). The C_{60} cluster has been shown to be particularly stable (Kroto et al., 1985), and has been postulated to be particularly relevant to the formation and morphology of soot (Zhang et al., 1986). It is unclear at this time if the C_{50} and C_{60} clusters observed in Figure 24 are "buried" in the original precipitates and are observable only after the surface has been removed, or are being

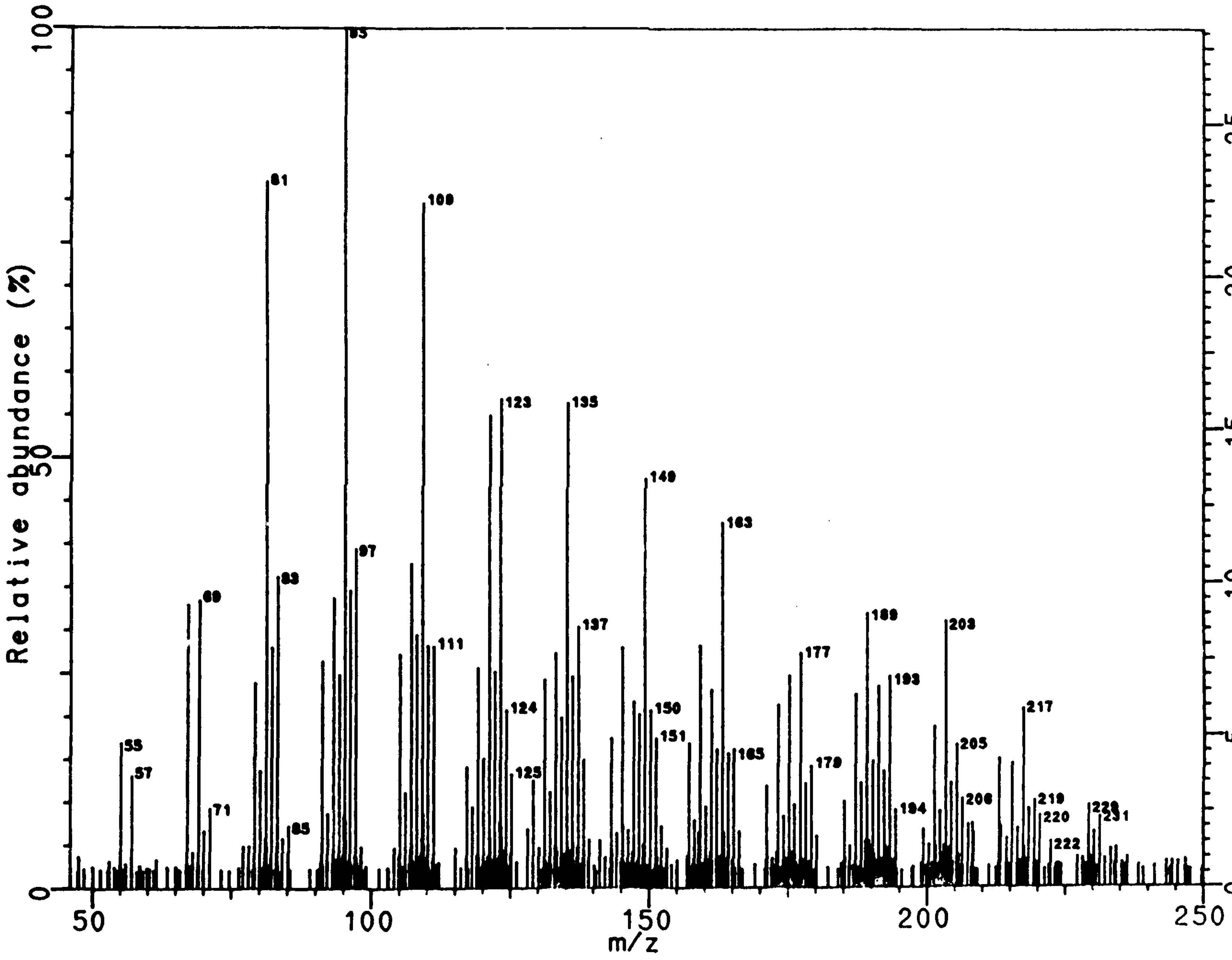

Figure 23. Stick Plot Mass Spectrum of Material Observable After Multiple Laser Strikes.

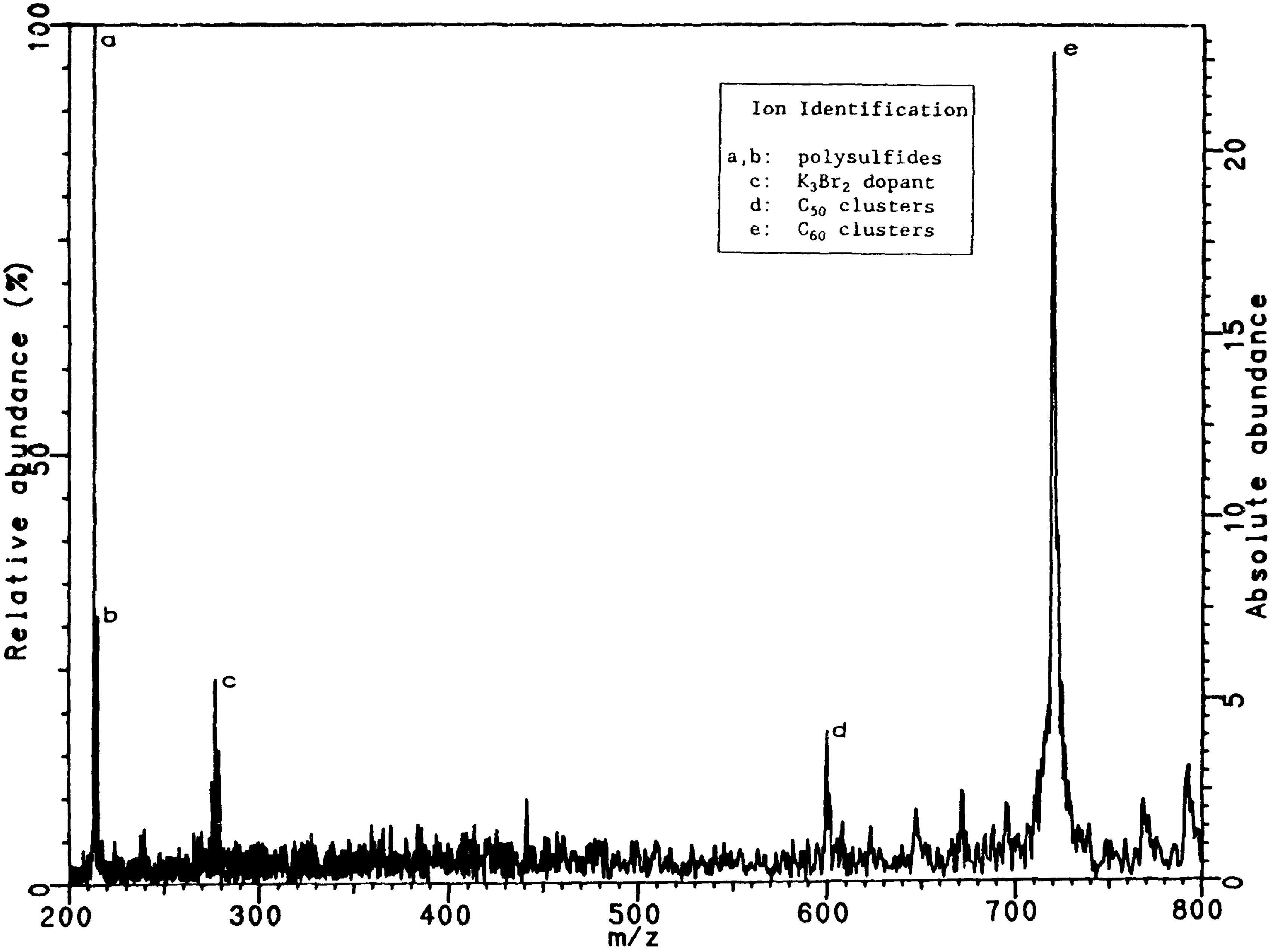

Figure 24. Higher Mass Range Spectrum Appearing After Multiple Laser Strikes.

formed in the sample by the repeated laser heating. Determining the source of these large carbon clusters, and their import to the formation of solids in jet fuel is another area that will be investigated.

The results of these preliminary experiments using LDFTMS to examine jet fuel solids have shown that the solids contain such elements as silicon, sulfur and oxygen, confirming a portion of the results from other techniques evaluated. Water or hydronium ions also appear to be in abundance. There appear to be differences in the precipitated material as a function of the number of times the laser is allowed to strike the same area of the precipitate. This could be a function of depth, the fact that the more volatile materials are being carried away, or the result of chemical reactions caused by laser heating. However, the solid deposits at different locations appear to be similar. The solid materials appear to contain large polysulfides, which could mean that solids would be more likely to form in fuels high in sulfur content. The presence of large carbon clusters is of particular interest due to the similarities in the formation of jet fuel particulates to the formation of soot. The presence of polyunsaturated or cyclic oxygen compounds is consistent with the hypothesized mechanism for fuel degradation.

Additional experiments are planned to determine the relevance of carbon clusters and the formulation of the suspected polysulfide. Experiments are also planned to coordinate LDFTMS with Fourier transform infrared spectroscopy analyses of solids formed under different conditions. A method for better mass calibration to allow more accurate mass measurement is being developed.

Liquid-Phase FTIR Studies

Studies by Bol'shakov (1972) indicate that Fourier Transform Infrared Spectroscopy (FTIR) may be a useful technique in monitoring changes in organic functional groups due to thermal stressing. This optical technique can monitor changes in organic functional groups and provide a quantitative measure of these changes. FTIR analyses were performed on liquid samples that had previously been stressed at a constant temperature in a batch microreactor. FTIR analyses have also been performed in situ as a sample of JP-8 fuel was stressed at 185°C at ambient pressure with oxygen bubbled through the liquid. Preliminary interpretation from these in situ analyses indicate that significant changes occur in the functional groups considered to be important in the fuel oxidation and degradation process (i.e., carbonyl groups, alcohol groups, ethers, etc.). However, FTIR analyses performed on samples stressed in the batch microreactor showed only minor changes, although significant sediment and darkening of the liquid were apparent from visual observation. These apparent inconsistencies are being investigated. If FTIR analyses can detect changes in these organic functional groups as a fuel is thermally stressed, this optical technique will be integrated with other instrumentation in the Thermal Stress Cell.

4. Summary and Evaluation of Instrumentation Techniques

Instrumentation techniques have been evaluated for use in acquiring data for the coupled flow, heat transfer, mass transport, and chemical processes occurring as jet fuel is thermally stressed. Consideration of the processes occurring indicate that fluid velocities, temperatures, gas-phase compositions, liquid-phase compositions, particle sizes, solid-phase compositions, and deposit mass accumulation are among the most important characteristics to be monitored to obtain the data necessary for model development. Laser Doppler velocimetry has been identified as the technique initially proposed for measuring fluid velocities. Thermocouples are presently judged adequate for measurement of temperatures in the Thermal Stress Cell. Evaluation of techniques for particle size measurements indicate that photon correlation spectroscopy is the preferred technique. An acoustic plate mode device is currently being developed and evaluated to measure in situ mass accumulation on a metallic surface. All of these techniques can provide quantitative information that may be required for model development. A variety of techniques appear useful to determine compositional and structural characteristics of solid deposits, including secondary ion mass spectroscopy with ion beam depth profiling, Auger electron spectroscopy, energy dispersive x-ray fluorescence, Fourier transform infrared spectroscopy, and laser desorption/ionization Fourier transform mass spectrometry. Many of these techniques, however, yield primarily qualitative information; no single technique can yield the quantitative information required for model development. A combination of techniques will be used until sufficient results are available to eliminate some of the techniques as non-useful. Fourier transform mass spectrometry is of potential use as a technique for monitoring in situ changes in liquid phase composition but further evaluations are necessary to determine the degree of quantitative data that can be produced. The appropriate optical techniques are being integrated with the Thermal Stress Cell for in situ measurements.

VI. NUMERICAL ANALYSES

A primary objective of this program is the development of predictive models for fuel degradation and deposition in a heated-flow environment. Because the mathematical models required to simulate a coupled fluid dynamics-heat transfer-mass transport-chemistry system will result in a system of partial differential equations, numerical codes must be used to solve the equations. Although commercial codes are available that can solve these equations, the codes require system-specific models of the chemistry under consideration, specified boundary and initial conditions for the particular problem defined, a description of the system geometry, and values for the liquid, solid, and gas properties and other system parameters. Presently, the most difficult aspect of the problem is the lack of definition of the chemistry involved in fuel degradation and solid deposition and the subsequent lack of mathematical models to describe those processes. Some simplified chemistry models have been proposed (Roquemore et al., 1989, Krazinski and Vanka, 1989; Deshpande et al., 1989), but are recognized as inadequate. However, numerical analyses using those models have qualitatively simulated flow experiment data (Roquemore et al., 1989, Krazinski and Vanka, 1989).

To obtain a computer code that has the general capabilities necessary to address problems involving fluid dynamics, heat transfer, mass transport, and chemistry, three options are available. First, a commercially-available code that possesses these general capabilities can be acquired and models specific to the system chemistry encoded. Examples of these commercial codes are (1) Phoenics (CHAM, Inc.), (2) FLOW3D (FLOW3D, Inc.), and (3) FLUENT (CREARE, Inc.). Disadvantages of these codes generally include a lack of efficiency with respect to the particular problems being investigated, a lack of flexibility in modifying the code, and the lack of an in-house expert on the structure and numerical solution schemes of the code. The second option is to use a code that solves a subset of the equations desired and modify the code. For example, a code that solves coupled fluid dynamics and heat transfer equations could be modified to include mass transport and chemistry. This option suffers many of the same disadvantages as using a commercial code that includes all of the general equations; however, an advantage is the familiarity of the code developer with the structure of the code involving the models of primary interest (i.e., the chemistry and mass transport models). The third option is to completely develop the code in-house. Although more resources are required, the advantages are that the code can be tailored to the problems under investigation, the code developer is available to solve problems associated with code structure and numerical solution schemes, and flexibility in modifying the code as model development proceeds. Work on these latter two options has been proceeding within the program.

Numerical analyses have been performed both to investigate the sensitivity of solids deposition to various model parameters and to provide benchmark calculations for verifying codes developed for this program. The former set of analyses used a code, FLANELS-2D, that has been modified for simulating fuel degradation and solids deposition in a heated, flowing system (Krazinski and Vanka, 1989). These preliminary sensitivity analyses were performed to ascertain the parameters that should be most tightly controlled and measured and to determine what type of diagnostic instrumentation would be required to perform those measurements. The set of benchmark analyses used a commercially-available fluid dynamics-heat transfer code, FIDAP (Fluid Dynamics International, Inc.). Benchmark calculations were performed to provide a set of fluid dynamics-heat transfer calculations that could be used to support verification of codes developed within the program. The code used, FIDAP, has received extensive checkout and should provide reliable results with which other codes used in the program can be compared to determine if they are accurately performing the numerical calculations.

The version of FLANELS-2D used included a chemistry model that described a one-step reaction in the liquid phase to form deposit precursors, followed by one-step reaction for deposition of the precursors on the surface. The formation of the deposit precursors was assumed to have an Arrhenius form with a linear dependence on oxygen and fuel concentration. The transport of precursors to the surface included a Fickian diffusion process using a single-valued diffusion constant for both oxygen and deposit precursors.

A. SENSITIVITY ANALYSES

Numerical analyses investigating parameter sensitivity were run using a simple tube (cylindrical) geometry, simulating conditions often used in flow tests. See, for example, Marteney and Spadaccini, 1986, Vranos et al., 1981. A constant heat flux enters the tube, with the value of the heat flux set to yield fluid temperatures less than 400°C, which is approximately the temperature at which autoxidation reactions (Hazlett et al., 1977) still dominate pyrolytic reactions and the proposed chemistry model is valid. The parameters investigated include velocity, temperature, diffusion coefficient, activation energy, and oxygen concentration. Because of the recognized inadequacies of the model used, the results of the sensitivity analyses should be used only for qualitative purposes. The results were used here to formulate criteria for design of the Thermal Stress Cell (see Section V) and to determine the types of diagnostic instrumentation that might be required.

As expected, temperature is a primary factor affecting fuel degradation and solids deposition. Because of the assumed Arrhenius rate formulation, reciprocal absolute temperature is logarithmically proportional to the deposition rate. This suggests that the temperature should be tightly controlled during kinetic experiments. Because of the effect that the flow regime (laminar versus turbulent) has on heat transfer and the potential transport of mass, fluid flow rate or velocity also has a significant effect on the solid deposition rate. These factors were important in developing the concept of a static cell experimental apparatus, where temperature and velocity gradients could be approximately eliminated, in which to develop kinetic models.

The sensitivity of deposition rate to parameters in the rate equation were also investigated. Because the concentration of precursors in the hypothesized model depends only linearly on the oxygen concentration, the solid deposition rate also depends linearly on the oxygen concentration. Experimental data (Taylor and Wallace, 1967) also show the importance of deposition rate on oxygen and suggests the need to accurately measure the concentration of molecular oxygen or oxygen containing functional groups in the liquid phase. As might be expected, the values of the activation energy and pre-exponential constant in the Arrhenius liquid-phase reaction rate also have a significant effect on the solids deposition rate. The dependence is again nonlinear. Marteney and Spadaccini (1986) performed flow experiments to determine an activation energy of approximately 40 kcal/mole for the liquid-phase reaction. Using that value, Roquemore et al. (1989) qualitatively simulated the dependence of deposition rate on temperature for flow experiments performed by Marteney and Spadaccini. However, because of the difficulties in measuring fluid temperatures, the temperatures used by Marteney and Spadaccini to determine the activation energies were wall temperatures. FLANELS-2D was used to calculate corresponding average fluid temperatures; these values were used to re-calculate an activation energy value. The value obtained, 31 kcal/mole, is similar to a value reported by Giovanetti and Szetela (1986) and is significantly different than the value reported by Marteney and Spadaccini. Subsequent numerical calibrations of the FLANELS-2D model showed that indeed a value of approximately 30 kcal/mole yields a better fit of the model predictions to the measured deposition rate values. These results show not only the importance of developing validated kinetic models but also show how numerical analyses using these models can be used to interpret data and supplement experimental measurements.

Analyses also indicated that the value of the diffusion coefficient used could significantly affect the solid deposition rate. Although a single value was used in the modeling for the diffusion coefficient, a distribution of values is expected under experimental conditions because of the distribution of particle sizes formed. See Section V. The importance of the value of this mass transport parameter indicated the need to measure in situ particle formation and growth and led to the choice of dynamic light scattering as the technique of choice for these measurements.

B. BENCHMARK ANALYSES

Benchmark analyses have been initiated involving both flow and heat transfer. These analyses can be used to support verification of the numerical accuracy of the fluid dynamics and heat transfer portions of codes developed for this program. All cases are for two-dimensional flow of an incompressible, Newtonian fluid over a backward-facing step with height equal to half the downstream channel height. Water properties are used for the fluid. Attachment points for recirculation regions are calculated as the basis for benchmark comparisons. Figure 25 shows a schematic of the general system geometry.

Two cases have thus far been completed. Case 1 has water at 25°C flowing through the channel and over the step, with the Reynolds number varied between 200 and 1200. Case 2 has a constant heat flux imposed on the lower boundary. Several heat flux values were imposed. Reynolds numbers of 100 and 800 were imposed. The reattachment points for both cases are presented in Table 5. Note that the upper recirculation zone is not present in all cases.

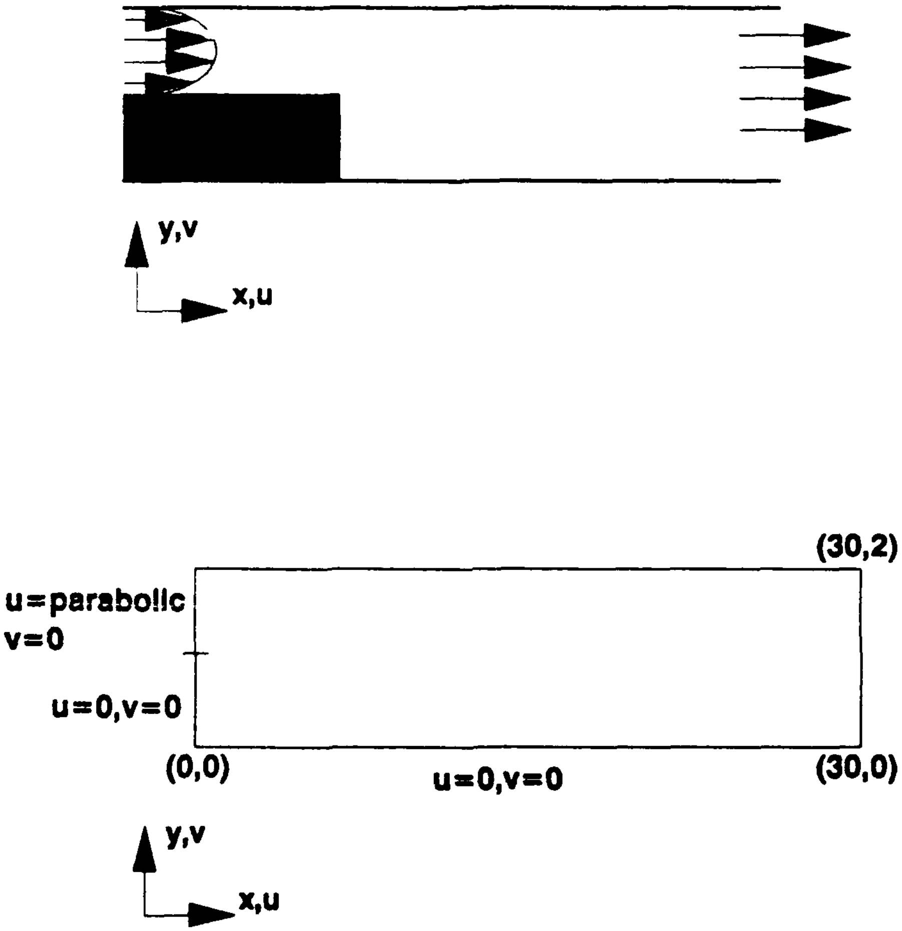

Figure 25. Backward-Facing Step Flow Geometry and Computational Domain.

Table 5. Attachment Point Values for Recirculation Zones as a Function of Reynolds Number

Case 1: Isothermal Flow

Re	x_0	x_1	x_2
200	5.32	--	--
300	7.19	--	--
350	7.89	--	--
365	8.13	--	--
375	8.37	8.25	9.25
380	8.37	8.13	9.65
400	8.61	8.04	10.46
500	9.82	8.32	13.50
600	10.79	8.75	16.20
700	11.48	9.20	18.77
800	12.19	9.66	20.83
900	12.89	10.20	23.20
1000	13.54	10.76	25.53
1100	14.05	11.20	27.19
1200	14.57	11.70	29.27

Case 2: Constant Heat Flux

Re	Q_{wall}	x_0	x_1	x_2
100	0.0	3.2432	--	--
100	0.3029	3.2696	--	--
100	0.6058	3.4017	--	--
800	0.0	12.188	9.664	20.827
800	4.5	12.188	10.300	20.693
800	7.0	12.278	10.300	20.693
800	15.0	12.554	10.628	21.096

VII. SUMMARY AND CONCLUSIONS

The development of advanced, thermally stable aviation fuels and methods to predict the stability of these fuels under varying operating conditions has been prompted by the anticipated increases in the thermal loading applied to fuel systems in high-performance aircraft. Prediction of the thermal stability of a fuel in an aviation fuel system requires mathematical formulations for the fluid dynamics, heat transfer, mass transport, and chemical kinetics of the system. General mathematical models for fluid dynamics, heat transfer, and mass transport have been established although values for the model parameters are system dependent. Models for the chemical kinetics of jet fuel degradation and solid deposition processes are not available. Data must be obtained to develop these models. An experimental system must be developed that has the capability to acquire the necessary information. After kinetic models have been developed, the coupling between these chemical processes and the physical processes will be investigated to produce a model that can simulate the range of processes occurring in a flowing, thermally stressed aviation fuel system. This model will be incorporated into a numerical computer code to facilitate predictive capabilities.

To address the objective of developing a predictive model for fuel thermal stability, efforts in the first year of this program have focused on identifying the parameters for which values should be measured, evaluating and developing instrumentation to obtain those values, and designing and fabricating experimental apparatus by which experiments can be performed to develop kinetic models at the temperatures and pressures of concern. Based on literature information, numerical analyses, and preliminary data acquired from thermally stressing and analyzing jet fuel samples, parameters have been identified that appear to be important in the fuel degradation and solids deposition process. These parameters include fluid velocities, temperatures, gas composition, particle size formation and growth, and liquid-phase and solid-phase compositions and structure. Instrumentation techniques have been chosen that can provide data for these parameters. A Thermal Stress Cell that can thermally stress jet fuel under controlled conditions and has access for optical and non-optical in situ measurements has been designed and is near completion. The knowledge and experimental apparatus developed during the first year of the program provide a sound basis by which data that are necessary for developing predictive models of fuel thermal stability can be acquired in the second and succeeding years of the program.

VIII. FUTURE ACTIVITIES

Completion of the Thermal Stress Cell apparatus and integration of the chosen optical techniques with the apparatus will be performed during the initial stages of the second year of the program. Cell-characterization studies will be completed to insure that the cell can control convective flow to a minimal level. Kinetic studies will then be initiated by stressing jet fuel or jet fuel surrogates at different temperatures and under various oxidative conditions to develop kinetic models of the fuel degradation process, the formation and growth of particles, and, to a lesser extent, the resulting accumulation of solid deposits on a surface. These models will be integrated with numerical computer code development activities to provide a basis by which flow experiments can be developed and calibrated.

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U.S. Government Printing Office 548-076