DOE/PC/30292-2
PSI TR-267

SYNTHETIC-FUEL COMBUSTION: POLLUTANT FORMATION.

SOOT-INITIATION MECHANISMS IN BURNING AROMATICS

SECOND QUARTERLY REPORT

FOR THE PERIOD

1 JANUARY 1981 - 31 MARCH 1981

T. TANZAWA, R. H. KRECH and W. T. RAWLINS

APRIL 1981

PREPARED FOR THE

U. S. DEPARTMENT OF ENERGY
DIVISION OF ENERGY TECHNOLOGY
UNDER CONTRACT DE-AC22-80PC-30292

PHYSICAL SCIENCES INC.
30 COMMERCE WAY, WOBURN, MASS. 01801

DISCLAIMER

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ABSTRACT

This is the second Quarterly Technical Report in a research program to study soot formation in the combustion of aromatic hydrocarbons. Experiments will be carried out in a shock tube at 1300-2500 K, using a variety of optical diagnostics to study the kinetic behavior of reactants, radical intermediates, and products. The data will be interpreted using a computer model of the kinetics and dynamics of the reacting system. In this report, the performance of the vacuum and data collection systems is described, and some initial shock wave measurements are presented.

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1. INTRODUCTION

Although considerable progress has been made in recent years in understanding the phenomenology of soot formation in the combustion of hydrocarbon fuels,[1-3] relatively little attention has been focused upon aromatic fuels of the types commonly found in coal liquids.[4] In particular, the effects of gas-phase free radicals, formed during combustion, on the kinetics of formation of incipient soot particles have not been characterized. Accordingly, we have begun an experimental investigation of the detailed kinetics of incipient soot formation in the combustion and pyrolysis of aromatic fuels of the benzene, anisole, phenol, and pyrrole families in order to determine soot formation mechanisms and rate parameters.

In a previous report,[5] we reviewed the literature on the high-temperature chemistry of aromatic hydrocarbons. The majority of this literature pertains only to pyrolysis, and provides global data and characterizations of soot and soot precursors. However, in combustion processes, free radical species such as O, H, and OH may play an important role in the fragmentation of ring structures. Furthermore, fuel carbon is converted into products such as CO and CO_2. In combustion of heterocyclic species containing fuel nitrogen, NO is also formed. All of these species are amenable to detection using optical spectroscopic techniques. Thus, combustion experiments in which the temporal behavior of these radical intermediates and products is observed, together with that of both fuel and soot, should provide valuable data on the chemical pathways leading to soot formation.

The objective of this research program is to experimentally examine the effects of gas phase free radical chemistry on soot initiation times in the combustion and pyrolysis of aromatic fuels such as benzene or toluene, and to extend the data base to more complex, heterocyclic species such as pyrrole, phenol, and anisole. The experiments will be performed in a shock tube over the approximate temperature range 1300-2500 K, with emphasis on the lower temperatures representative of industrial applications. Kinetic interpretation of the data will be carried out via computer simulation of the chemical and physical processes occurring behind the shock front. The

details of the experimental design and kinetic modeling were described in the previous Quarterly Report.[5]

During the present reporting period, the final assembly and shake-down of the shock tube apparatus, with its associated vacuum and electronic systems, has been completed. In the following discussion, the operation of the shock tube facility and the data acquisition system are discussed in Section 2, and the results of some initial shock wave measurements are described in Section 3. A progress summary and plans for the next quarter are presented in Section 4.

2. EXPERIMENTAL

The experiments will be carried out in the shock tube apparatus shown schematically in Fig. 1. The optical and pressure observations will be made in incident shock waves at temperatures between 1300 K and 2500 K. Typical experimental conditions will employ Ar/fuel/O_2 test gas mixtures containing > 90% Ar at pre-shock pressures of ~ 20 torr. Attainment of the desired temperature range will require shock velocities of Mach 4-5 (1.3-1.6 km/s in Ar); the resulting test gas pressure will be 400-600 torr. These conditions can be attained using H_2 as a driver gas at pressures of 1.7-4.2 atm. Driver gas bursting pressures are controlled by selection of appropriate diaphragm thicknesses. The design of the shock tube and associated gas handling lines, the calculation of the required shock conditions, and the general design of the optical diagnostics were presented previously.[5] In the following sections we describe the finished vacuum system, procedures for sample preparation, operation of the shock tube, and the data processing and acquisition system.

2.1 Vacuum System

A schematic diagram of the complete experimental vacuum system is shown in Fig. 2. The driver section is connected with the high-pressure control line through the flexible stainless steel hoses which allow separation of the driver and test (driven) sections while changing diaphragms. The high-pressure driver gas control line is of conventional design with 1/4-inch stainless steel tubing and fittings. All flow regulating valves are rated for maximum operating pressures of 500 psig. The diaphragm bursting pressure is monitored by a 6-inch bourdon gauge (Matheson, 550 psig). A high-pressure regulator attached to the hydrogen cylinder limits the line pressure to values below the limit of the Matheson pressure gauge. When high-pressure hydrogen gas is introduced to the driver section, the operation is carried out remotely on the driver gas control panel, shown in Fig. 2. The high-pressure system is evacuated by a 100 ℓ min^{-1} Kinney rotary pump. Pressures below 1 torr are monitored by Varian 531 thermocouple gauges.

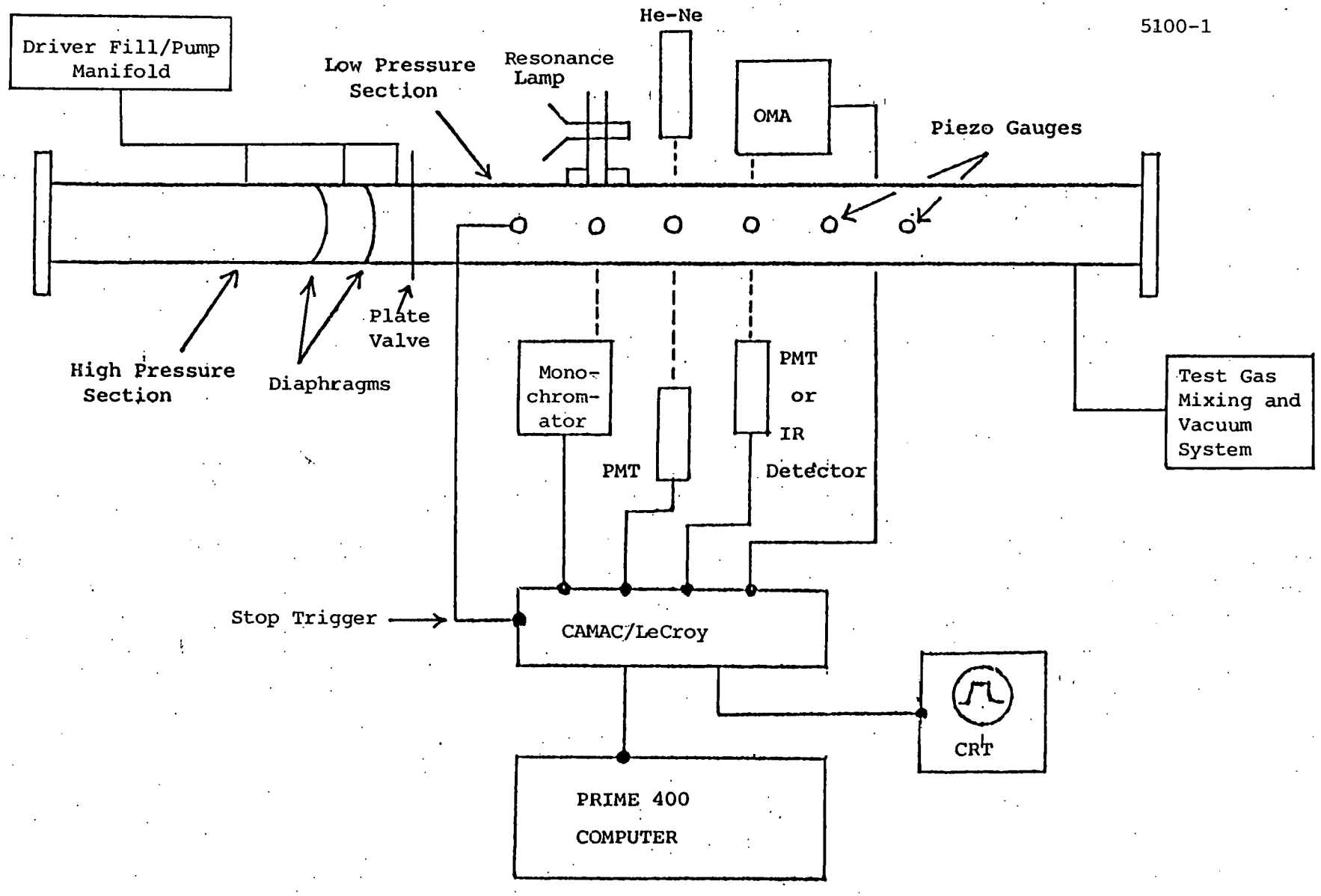

Fig. 1 Schematic of shock tube apparatus, illustrating some of the optical and pressure diagnostics. PMT = photomultiplier; OMA = optical multichannel analyzer (diode array + monochromator) for use in spectral surveys.

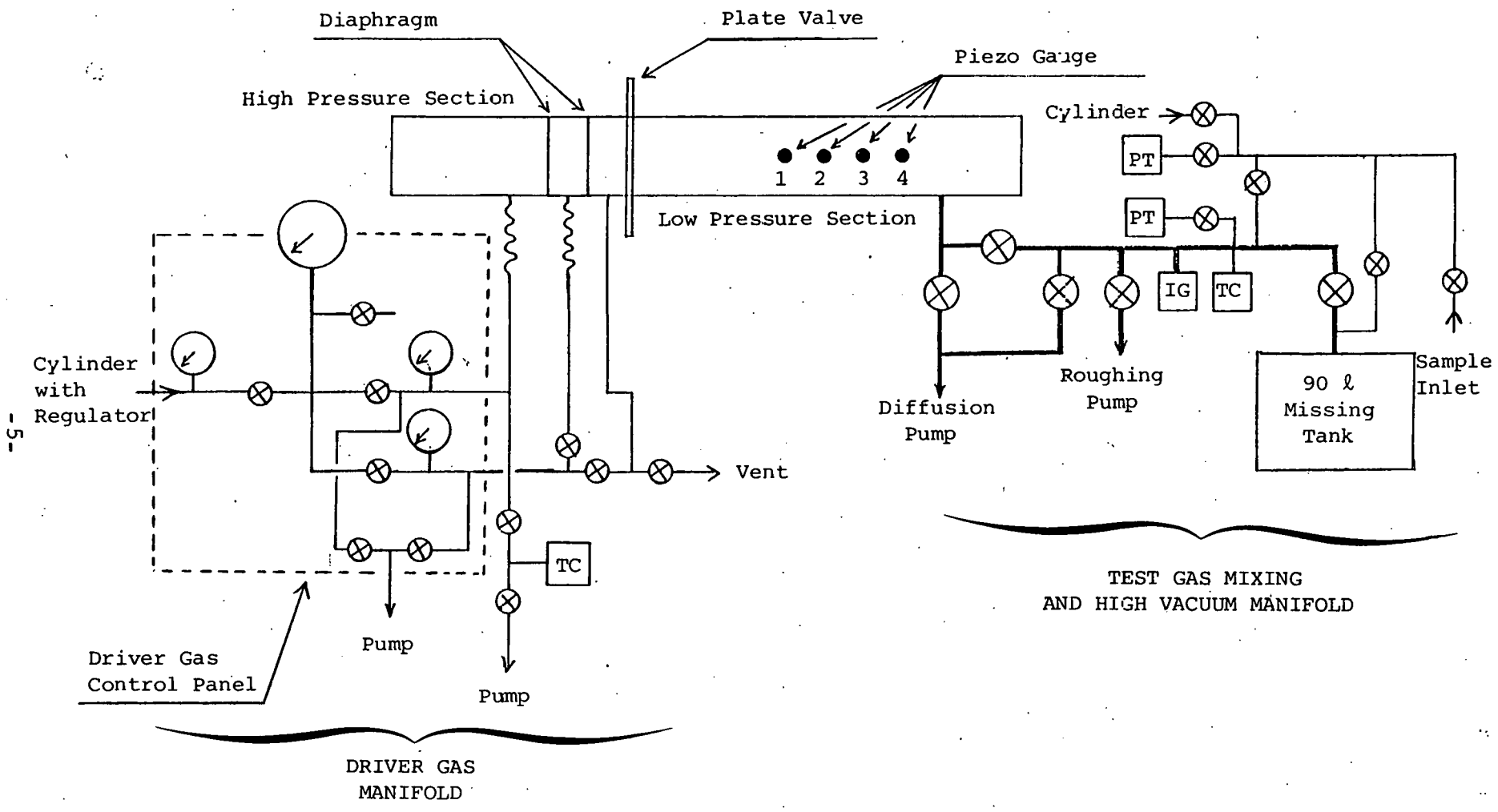

Fig. 2 Schematic diagram of vacuum line assembly: IG - Ionization Gauge; TC - Thermocouple Gauge; PT - Pressure Transducer. Dashed line indicates the high pressure control panel operated remotely about 3 m away from the high pressure section.

During this reporting period, we installed the plate valve shown in Figs. 1 and 2, and tested it successfully. This valve allows isolation and evacuation of the low pressure section while changing diaphragms, thus reducing the pumpdown time between experiments.

The vacuum line for the low-pressure test section (cf., Fig. 2) is connected to the shock tube near the end plate. The main vacuum manifold consists of 1- and 1/4-inch (O.D.) stainless steel tubing and one-inch brass bellows valves. The sample gas inlet manifold consists of 3/8-inch (O.D.) stainless steel tubing and stainless steel bellows valves. All tubing used in this system was carefully passivated with 25% nitric acid solution. The shock tube test section, the vacuum manifold, and the 90 ℓ mixing tank are evacuated through a liquid nitrogen cold trap by a two inch diffusion pump, (Consolidated Vacuum Corporation Type PMC520, Dow-Corning 704 silicone diffusion pump fluid), backed by a 100 ℓ min^{-1} Welch-Duoseal forepump which also serves as the roughing pump. This pumping system is capable of evacuating the shock tube test section from 1 atm to 10^{-5} torr in approximately 25 min. Pressure is monitored with a Varian 571 ionization gauge ($10^{-8} < P < 10^{-4}$ torr), Varian 531 thermocouple gauge ($10^{-4} < P < 1$ torr) and two Validyne DP15-30 and -42 pressure transducers ($0 < P < 60$ torr, $0 < P < 1000$ torr, respectively). The former two gauges were calibrated using a McLeod pressure gauge; the Validyne pressure transducers were calibrated using mercury and oil manometers.

The shock tube test section, the vacuum manifold, and the 90 ℓ mixing tank were thoroughly leak-tested: the present leak rates are 10 μ/hr, 50 μ/hr, and 10 μ/hr, respectively. These leak rates are acceptable for our initial experiments; however, the latter two values are high enough to limit the storage time for gas mixtures. We will continue efforts to reduce these leak rates further.

Test gas mixtures, e.g., toluene/argon, are prepared at 1-5 atm total pressure in the 90 ℓ mixing tank shown in Fig. 2. The diluent gas is ultra-high purity Ar (99.999%) from Union Carbide Corporation, and is used without further purification. The toluene is Spectranalyzed grade from Fisher

Scientific Company. Before admission to the mixing tank, toluene is thoroughly degassed by a repetitive freeze-and-thaw technique using liquid nitrogen. The mixtures are prepared manometrically using Validyne pressure transducers and are stored in the mixing tank for 24 hours prior to experiments to assure complete mixing.

2.2 Operation of Shock Tube

The experimental sequence for firing a shock is as follows. The test section is loaded with a test gas mixture to ~ 10-30 torr, as measured by the Validyne pressure transducer. The vacuum manifold is isolated by closing the valve immediately connected to the tube as shown in Fig. 2, and then the diaphragm is ruptured using either the single or double diaphragm technique, as described in our previous report.[5] After each experiment, the plate valve is closed. The portion of the shock tube upstream of the plate valve is first cleared of hydrogen driver gas and of possible toxic fumes by pumping it to less than 1 torr with the roughing pump. The tube is then filled to atmospheric pressure with dry nitrogen and opened, and the diaphragm(s) is(are) changed. Meanwhile, the downstream portion of the tube and the vacuum manifold are evacuated. After evacuating the upstream side of the plate valve, the plate valve is opened, and then the whole low pressure section and the vacuum manifold are evacuated to 10^{-5} torr or less for a subsequent experiment.

Diaphragms are prepared from 0.01-0.06 in. thick 3003-H14 alloy aluminum sheet. To facilitate rupture, they are pressure-scored with a four-petal design. This is accomplished by a 1/2-in flat steel scoring plate with four steel wires (0.014 in diameter) stretched in a cross pattern. The aluminum diaphragm sheet is pressed between the scoring plate and a flat back plate in a hydraulic press at pressures up to 7500 psi. Variation of the diaphragm thickness and scoring pressure allows coverage of a wide range of bursting pressures, and, hence, selection of the desired shock temperature.

2.3 Diagnostics and Data Acquisition

The four inch shock tube shown in Fig. 1 is used to rapidly heat synfuel analogs to temperatures where sooting is likely to occur during combustion. During each test, pressure and optical measurements are made in the shock heated gas. Piezoelectric pressure transducers mounted on the tube wall measure the gas pressure and are used to determine the shock velocity; the velocity is later used to calculate the gas temperature. In addition, a variety of photodetectors is used to monitor emission and absorption in the hot gas. Photomultipliers and silicon photodiodes are used in the ultraviolet and visible regions of the spectrum and indium antimonide detectors are used in the infrared; these detectors yield both quantitative and qualitative information about the chemical species involved in the combustion processes. In each experiment, the shocked gas is heated virtually instantaneously (several molecular collisions), but remains hot for only a few milliseconds. All measurements must be conducted within this time frame, and therefore shock tube experiments require instrumentation with microsecond response times.

Traditionally, shock tube data have been collected by photographing a trace from an oscilloscope screen. Analysis of these traces is very time-consuming, since each trace must be individually analyzed and measured with calipers to extract the most accurate information. Advances in digital electronics over the past decade now allow extremely rapid conversion of analog instrumentation signals into a digital format which can be stored and read into a computer. In these experiments, we use a state-of-the-art data acquisition system to collect and store experimental data.

The PSI computerized data acquisition system is based on the CAMAC (Computer Automated Measurement And Control) protocol. CAMAC is an international standard of modularized electronics as defined in IEEE-Std-583-1975, and has been adopted as the primary instrumentation interface by the National Laboratories. Our CAMAC system is interfaced to a PRIME 400 mainframe, and utilizes a modified version of the PRIMOS REV 15 operating system developed by Los Alamos National Laboratory, which allows all systems commands to be written in FORTRAN.

The shock tube data acquisition system is built around two LeCroy Model 8210 Multichannel Waveform Digitizers. Each unit can simultaneously sample four analog signals at a 1 MHz rate, and has a 32 K word memory that will store 8 milliseconds of data. For the full 10 bit accuracy (0.1%), an input voltage swing of 10 volts is required. Few real signal levels exactly match the input requirements of the digitizers, so instrumentation amplifiers must be used to boost the observed signals to the desired levels. Amplifiers for the pressure transducers, stop-trigger generation and shock speed measurements are designed and built in house. Typical circuits for these amplifiers and examples of input and output waveforms are shown in Figs. 3 and 4. For more conventional signal amplification, two LeCroy Model 8100 Dual Programmable Differential Amplifiers are available with a variable gain of 0.2 to 100. Low level photomultiplier signals can be initially amplified by a LeCroy Model 612AM 6 Channel Photomultiplier Amplifier.

Operation of the system is straightforward. Before a test the digitizer start buttons are depressed. Each digitizer continually converts the analog instrumentation signal to digital values and stores the output in the digitizer memory. The memory is updated continually, retaining the previous 8 milliseconds of signal. When the shock travels down the tube, the pressure rise is detected by the pressure transducers and a stop trigger pulse is generated from one of the transducers. This pulse commands the digitizers to stop taking new data after a preset time delay. In this way, the desired test information is retained in the digitizer memory. A FORTRAN program "WAVEFORM" then transfers the information from the digitizer to the computer's central disc files. Plots of the data are immediately generated on a Tektronics 4006 graphics terminal located in the shock tube control room. Hard copies of these plots and listings of the digital data are obtained from the computer output terminal. The data files are transferred from the disc system to magnetic tape and kept as a permanent record of the test; all test data are then available for future analysis. Example pressure transducer data are discussed in Sec. 3.

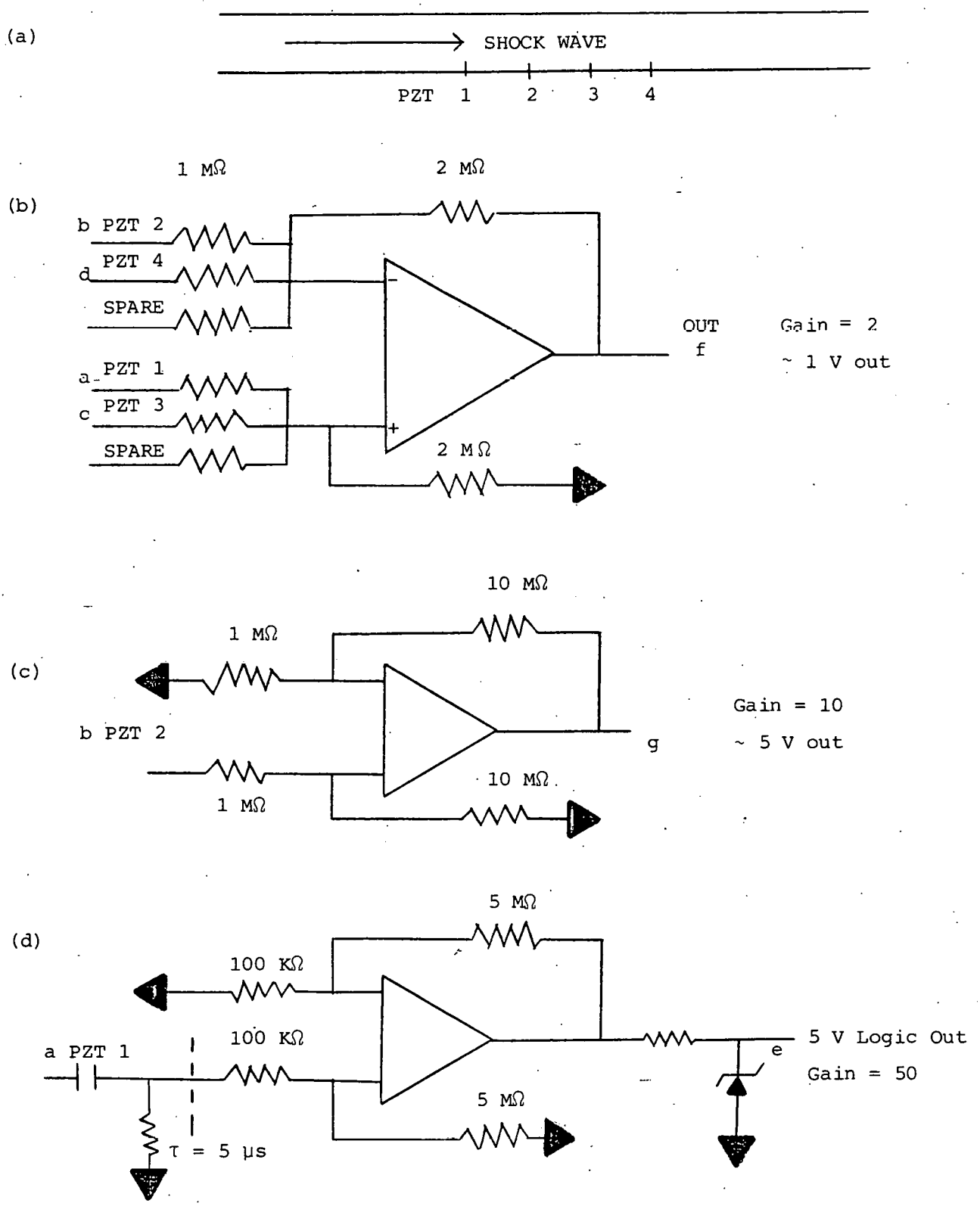

Fig. 3 Piezo gauge signal processing. (a) Position of piezo gauges (PZT) in shock tube. Transducer sensitivities are 40-50 mV/psi. (b) Speed system multiplex and amplifier circuit. (c) Pressure monitor circuit. (d) Stop trigger amplifier. The data stop delay is initiated by a pressure increase greater than 1 psi in 5 μs.

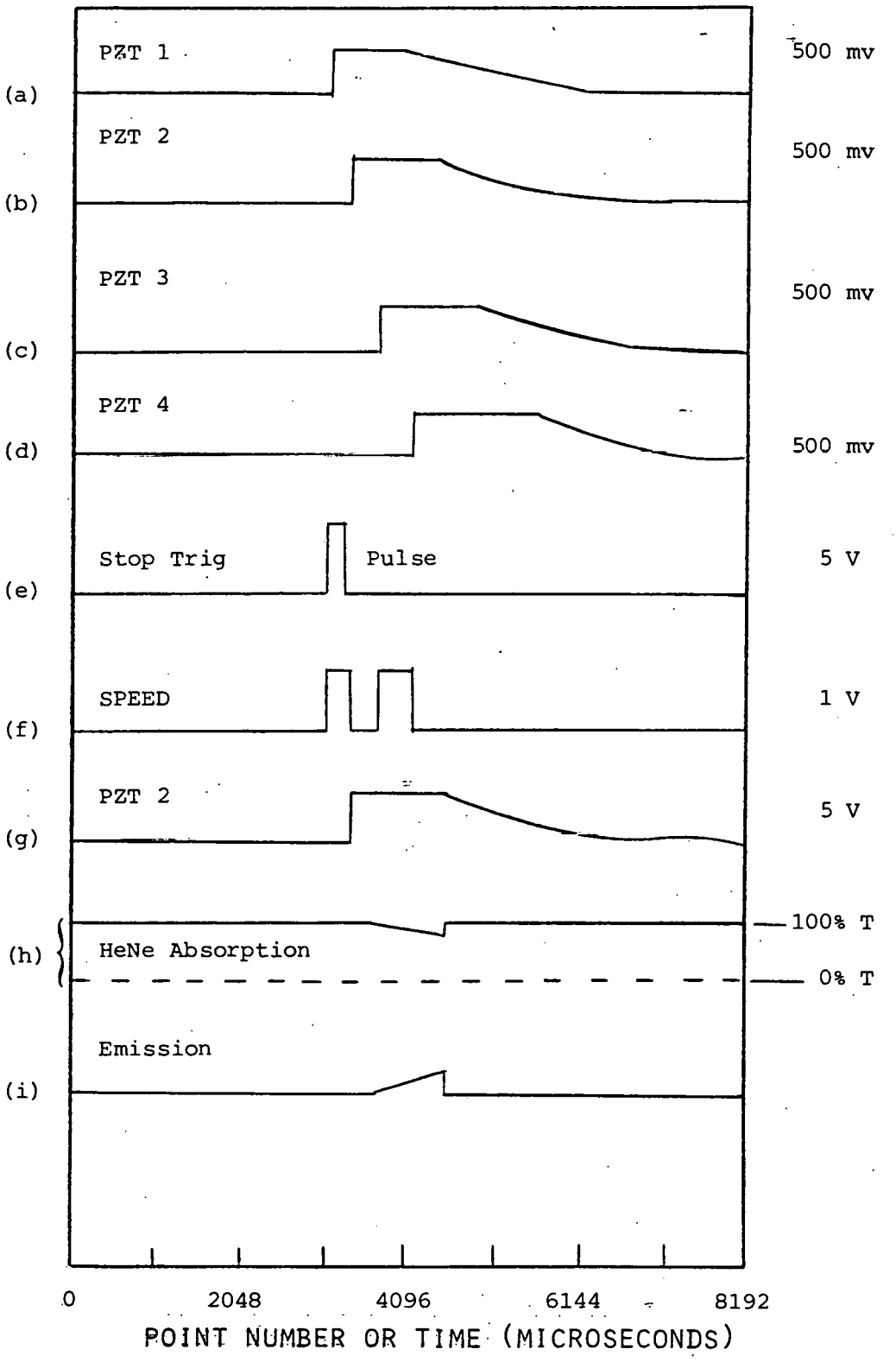

Fig. 4 Idealized shock signals for various diagnostics. (a)-(d). Individual pressure probes, unamplified. (e) Stop trigger pulse. Data stop delay is ~5 ms. (f) Amplified shock speed data. (g) Amplified pressure data. (h) Optical signal, absorption measurement. (i) Optical signal, emission measurement.

3. SHOCK WAVE MEASUREMENTS

3.1 Pressure Profiles and Shock Wave Velocities

The test gas pressure history before and after passage of the incident shock wave is monitored at four piezoelectric gauge stations (PCB-Piezoelectronics, Inc., 111-A21) placed at 25.4-cm intervals. Typical pressure profiles (in Ar) from each station are shown in Fig. 5. The arrival of the incident shock wave at each station is seen as a sharp pressure rise followed by a constant pressure region. The detailed pressure profile from the #3 piezo gauge is shown in Fig. 6. The pressure is constant over approximately 600 μs, and then begins to decrease slowly due to the arrival of the head of the reflected rarefaction wave. After passage of the incident shock wave, arrival of the reflected shock wave from the end plate is seen in Fig. 5 as larger pressure jumps. These reflected shock pressure profiles are quite different from those we have seen behind the incident shock wave. This is because the reflected shock wave propagated at the positions of the piezo gauges is between the head and tail of the reflected rarefaction wave.

The arrival time intervals for the incident shock wave are used to calculate shock velocity, attenuation, and temperature as described in detail in our last report.[5] The four piezo gauge traces in Fig. 5 give three successive shock velocities of 1.17, 1.16, and 1.16 mm/μs, corresponding to incident shock conditions T_2 = 1470 K, P_2 = 480 torr, and $[Ar]_2 = 3.1 \times 10^{18}$ cm^{-3}. The slight decrease in velocity from one interval to the next indicates that the attenuation of the incident shock wave velocity along the tube was less than 0.5% over 25.4 cm. The observation time was approximately 600 μs, corresponding to 700 mm behind the shock front. Thus, a shock wave speed attenuation of 1.4% would be expected over our entire observation time. This 1.4% attenuation of the incident shock velocity corresponds roughly to a 0.7% decrease in temperature (about 10 K) between the beginning and the end of the observation. Attenuation of the shock wave velocity is due mainly to boundary layer growth along the tube and is a function of the volume

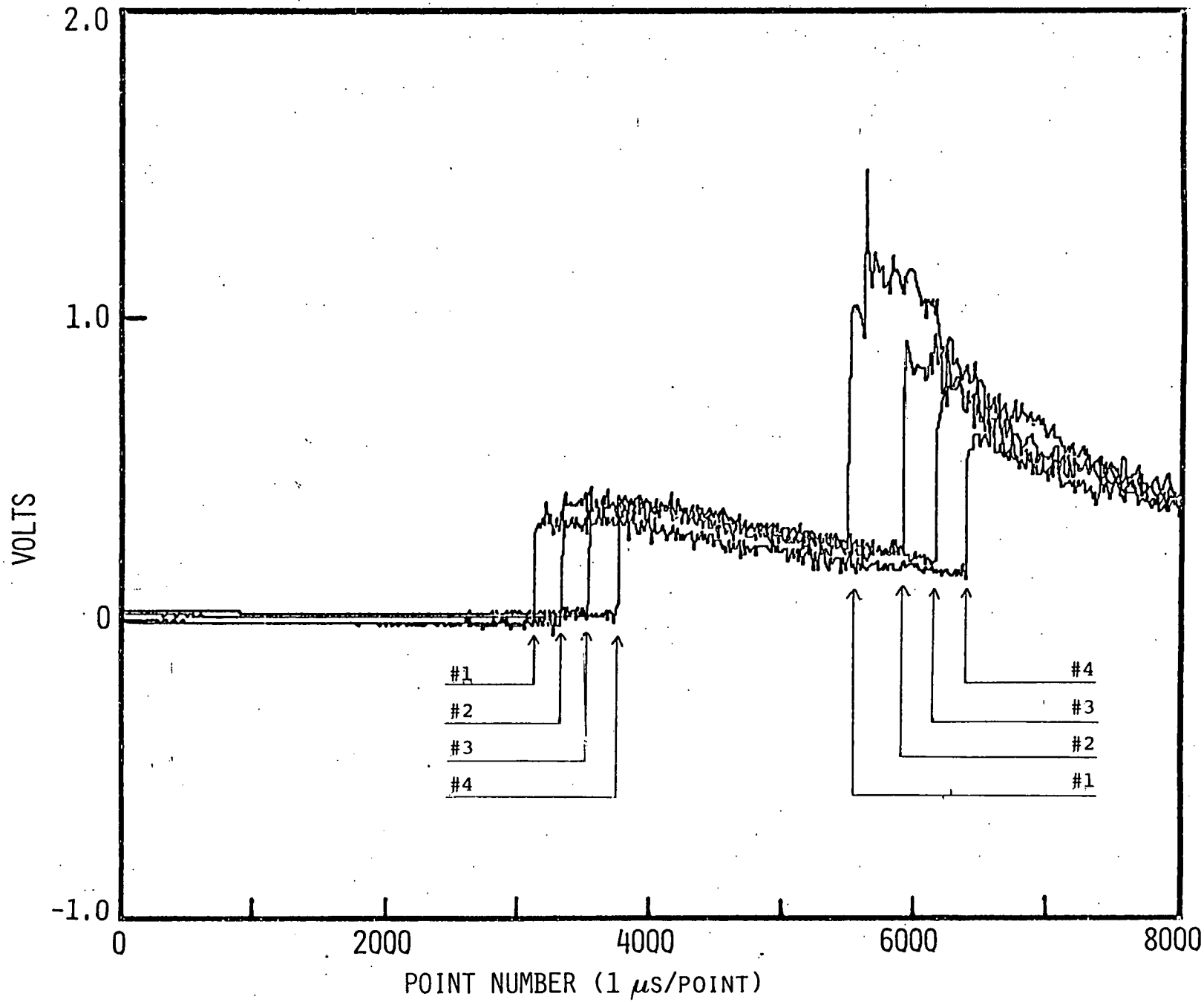

Fig. 5 Pressure profiles behind incident and reflected shock waves at each piezo gauge station for an H_2-driven shock into 30 torr Ar. Conditions behind incident shock wave are T_2 = 1470 K, P_2 = 0.63 atm, v = 1.16 mm μs^{-1}, and $[Ar]_2 = 3.13 \times 10^{18}$ molecule cm^{-3}. 50 mV corresponds to 1 psi and point number indicates a 1 μs time interval.

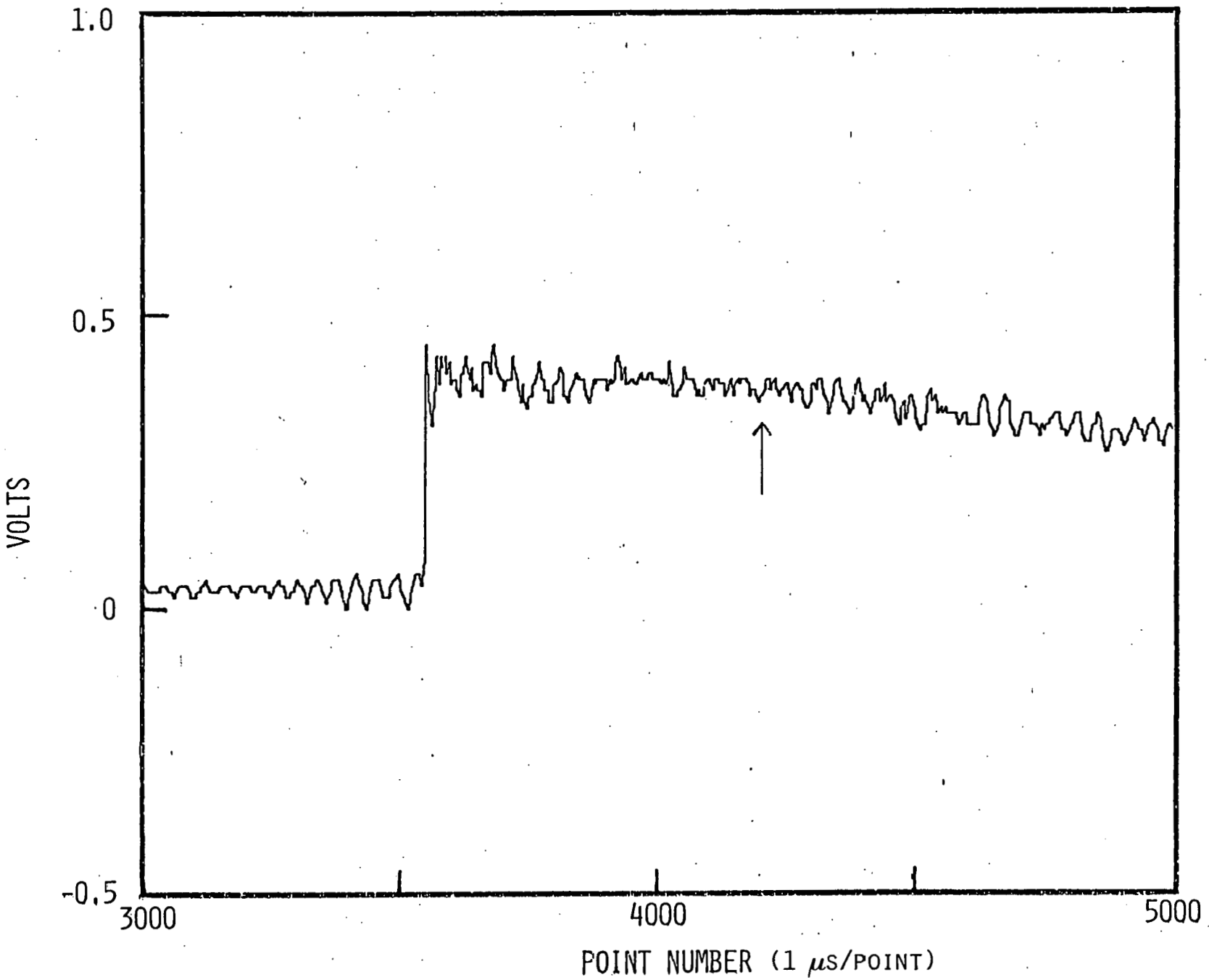

Fig. 6 The detailed pressure profile at #3 piezo gauge station from Fig. 5. The arrow indicates arrival of the head of rarefaction wave. The portion between the shock arrival and the arrow represents the useful test time, ~ 600 μs. The noise on the trace appears to be due to mechanical vibration.

ratio between the boundary layer and the core flow, i.e., the larger the shock tube diameter, the less the shock wave velocity attenuation. Thus, for the relatively large diameter of our shock tube (10 cm), the observed attenuation is small as expected. This is an important result because it confirms experimentally the feasibility of using optical diagnostics at several axial positions along the shock tube. Further measurements will be made to map the attenuation as a function of shock velocity; however, these preliminary measurements indicate that the temperature change due to shock attenuation is negligible compared to that expected from the combustion processes to be studied.

3.2 Laser Beam Attenuation Experiments

A He-Ne laser beam attenuation diagnostic has been set up to monitor appearance of incipient soot particles in aromatic fuel combustion. The 6328 Å He-Ne laser is a 1 mW Spectra Physics Model 155 (TM 00 mode) with a beam diameter of 1.2 mm at the aperture exit. The beam was directly focused normal to the shock tube axis. Care was taken in the beam alignment in order to: (1) optimize the spatial resolution; (2) avoid reflection of the beam from the windows back into the cavity, thus eliminating instabilities in the lasing action; (3) avoid window reflections onto the detector. The time (or space) resolution of this experiment is given by the ratio of the beam diameter to the shock velocity and is approximately 1 μs. The detector is an RCA 1P28 (S-20 spectral response) photomultiplier tube powered by an EMI GENCOM Model 3000 R high voltage power supply. A 6328 Å interference filter (10 Å bandwidth) and a diffuser were placed in front of the photomultiplier tube to protect from extraneous light and to diffuse the small laser beam uniformly onto the photocathode surface. In addition, to identify arrival of the shock front, a knife-edge, perpendicular to the shock tube axis, was placed in front of the interference filter; the knife-edge was positioned slightly outside of the laser beam. This knife-edge provides a sharp schlieren signal upon arrival of the shock front and allows clear identification of time-zero.

Prior to each experiment, the zero-transmittance level is determined by modulating the laser beam with a chopper mounted on the shaft of a 3000 RPM miniature motor; the chopper is then turned off and the shock is fired. The detector output is processed by the data acquisition system as described in Sec. 2.3. The components for this diagnostic are assembled and aligned, and initial soot attenuation experiments are in progress. Although some beam attenuation has been observed for toluene/Ar mixtures near 1400 K (a relatively low temperature for sooting), the electrical noise level is greater than expected. Work is now under way to identify and eliminate the cause of this noise and to extend the measurements to conditions more favorable to soot formation.

4. PROGRESS SUMMARY AND RESEARCH PLANS

The shock tube facility is now fully operational. All subsidiary vacuum lines have been assembled and leak-tested. Test shocks have been fired to characterize the diaphragm properties, test times, shock properties, and data acquisition. A laser absorption diagnostic for soot has been set up and some initial toluene pyrolysis experiments have been performed.

Plans for the coming quarter are directed toward diagnostic development and systematic studies of soot formation from aromatic hydrocarbons. We will continue to work on the laser absorption diagnostic and will begin setting up other absorption diagnostics for parent fuel, OH, and O, as well as several infrared and ultraviolet emission measurements. We will also begin a systematic series of experiments to map incipient soot points as functions of temperature, pressure, and mixture composition.

The program accomplishments to date are reasonably consistent with the original program schedule, and no major difficulties have been encountered. Contributing technical personnel during this quarter were T. Tanzawa, R. H. Krech, S. Schertzer, and W. T. Rawlins.

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