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NO. 1140

DETONATIONS IN HYDROGEN SULPHIDE-AIR CLOUDS (U)

by

A. Sulmistras*, I.O. Moen and A.J. Saber*

PCN No. 77C50

May 1985

* Mechanical Engineering Department, Concordia University, Montreal, Quebec.

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ABSTRACT

This paper reports on an investigation to determine the detonation hazards of hydrogen sulphide/air mixtures in relation to the detonation hazards of other more common fuel-air mixtures. Parameters which characterize the sensitivity of fuel-air mixtures to detonation are discussed. Theoretical and empirical relations between the various detonation parameters are also described, and the current status of detonation hazard evaluation is summarized. Finally, the results from a series of hydrogen sulphide/air field trials are used together with previous results and numerical calculations to determine the sensitivity of this mixture to detonation. It is found that hydrogen sulphide forms a mixture with air that is less sensitive to detonation than most common gaseous hydrocarbon fuels except methane.

SPONSORSHIP

The investigation described in this report is part of a project to characterize the explosion hazards of hydrogen sulphide, which is sponsored by the Atomic Energy Control Board of Canada. The present report is the second report on this project. A previous report entitled "Investigation of The Explosion Hazards of Hydrogen Sulphide" was prepared under contract by A.J. Saber of Concordia University.

ACKNOWLEDGEMENTS

Several colleagues and organizations contributed to the work described in this paper. We would particularly like to thank Dr. Joseph Shepherd of Sandia National Laboratories for performing the calculations which allowed us to tie all the results together, and professors John Lee and Rom Knystautas for giving us access to some of the unpublished results from McGill University.

The assistance of Mr. Gayle Hall and Mr. Stephen Ward in planning and carrying out some of the field trials is gratefully acknowledged. We would also like to thank the personnel of the Field Operations Section, the Electronic Design and Instrumentation Group, and the Photo Group at DRES for their valuable assistance during the field trials. The excellent safety course and advice given by Bryne Emeneau of AECL was instrumental in planning the safety procedures required for the field tests. We would also like to thank Mr. Stan Mellsen for performing the dispersion calculations which helped us establish safety distances for the trials.

Finally we would like to thank Dr. Paul Thibault and Professor Rom Knystautas for their input through enlightening scientific and technical discussions.

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1. INTRODUCTION

Many manufacturing and industrial plants store and use large quantities of flammable gases. For personnel and plant safety, it is therefore necessary to realistically assess the potential hazards from an accidental spill of these fuels. Of particular importance are the consequences if the spilled gases are ignited. If ignition occurs immediately, a diffusion flame will result and the rate of burning will be controlled by the mixing of the fuel with air. In this case, the hazards due to thermal radiation from the burning fireball are more important than blast effects. However, if immediate ignition does not occur, a potentially explosive fuel-air cloud will develop. This cloud will be fuel lean at the outer perimeter and fuel rich near the source. Depending on the nature of the ignition source and reactivity of the fuel-air mixture, such a cloud can either detonate or burn. Detonations are the most devastating explosions possible and are characterized by high velocities and high pressures. Flame velocities and flame pressures, on the other hand, depend on the obstacle configuration and flow field into which the flame propagates. An initially laminar flame in the presence of obstacles, for example, will accelerate and become turbulent with a corresponding increase in its velocity and pressure (1,2). Also, depending on the scale of turbulence and the flame speed, transition to detonation could occur (3,4). In order to assess the explosion hazards associated with a spill of a given fuel, one must first quantify the sensitivity of a given fuel-air mixture to detonation and transition to detonation.

Two key properties which characterize the detonability of an explosive mixture are: i) the critical energy, E_c, required to initiate detonation in the mixture, and ii) the critical tube diameter, d_c, required for a planar detonation emerging from a tube to transmit to an unconfined spherical detonation. These properties are intimately related to the chemical processes within the detonation wave. Due to the complexity of the detonation structure, these detonation parameters cannot yet be calculated from first principles. Experimental input is therefore required in order to characterize the detonability of an explosive mixture. Fortunately, theoretical and empirical relationships between various detonation parameters have recently been established, so that a number of experimental methods can now be used to determine the detonation sensitivity of a given mixture. A more complete discussion of detonation parameters and their interrelationships is given in Section 2.

Once it is assumed that the threat of detonation does exist, it is important to determine the blast effects. Detonation parameters, such as detonation velocity, pressure and temperature, can be calculated from equilibrium thermodynamic chemistry alone. Computer codes are readily available for this purpose (5). These equilibrium parameters provide the initial conditions for calculation of the complete blast field both inside and outside the detonation cloud. Considerable theoretical and numerical work in this area has been done for the Defence Research Establishment Suffield (DRES) by Thibault. This work is now at the point where accurate flow field predictions from fuel-air detonations can be made (6,7). Thus, once the potential for detonation and transition to detonation have been determined, a realistic estimate of the subsequent blast waves can be made.

The present paper reports on an experimental investigation to determine the sensitivity of hydrogen sulphide/air (H_2S/air) mixtures to detonation in relation to the sensitivity of other more common fuel-air mixtures. Hydrogen sulphide is a gaseous fuel at standard atmospheric conditions and is used in large quantities in the Girdler-Sulphide process for production of heavy water (deuterium oxide), which is an essential material for the operation of CANDU nuclear reactors.

Previous studies on detonations in H_2S/air were limited to confined detonation tubes (8) and the influence of confinement was not accounted for. However, some of the data from these tests do provide useful input to the assessment of the detonability when interpreted in the light of more recent developments (9).

A brief review of detonation parameters, their interrelationship and physical significance is given in Section 2. This is followed in Section 3 by a description of the experimental apparatus and diagnostic techniques used in the present experiments. The experimental results are presented and discussed in Section 4, and Section 5 contains the conclusion to this investigation.

2. DETONATION PARAMETERS

A detonation can be simply described as a coupled reaction zone-shock wave complex which propagates through a uniform combustible mixture at a constant velocity. The shock wave heats up the mixure to a temperature above the ignition temperature, thus providing the ignition source for combustion to begin, and the chemical energy released in the reaction zone provides the energy required to maintain the shock wave.

A one-dimensional model of the detonation wave, usually called the Zeldovich-von Neumann-Doring or ZND model, includes an induction zone separating the leading shock wave and the onset of chemical reaction (10). It is now known that the structure of detonations is in fact three-dimensional and includes waves moving transverse to the direction of detonation propagation. Nevertheless, the ZND model provides a useful first approximation to the detonation structure. In fact, many detailed chemical-kinetic models of detonations use the hypothetical ZND induction zone length to characterize the relative detonability of different explosive mixtures.

The parameters which are used to characterize a detonation include: i) the equilibrium properties (i.e., detonation velocity, pressure and temperature), ii) the minimum energy, E_c, required to establish a detonation, iii) the critical tube diameter, d_c, which characterizes the minimum size of a detonable cloud, and iv) parameters which characterize the structure of the detonation (i.e., the transverse wave spacing, S, or the ZND induction length, Δ). Detonation parameters for some common fuel-air mixtures at stoichiometric composition are given in Table I. Results for hydrogen sulphide/air mixtures which were obtained in the present study are also included in this table.

2.1 Equilibrium Properties

The velocity of a detonation can be calculated based on the total chemical energy released in the reaction zone without regard to how this energy is deposited. The corresponding pressure and temperature at the end of the reaction zone, or the so-called Chapman-Jouguet (C-J) point, can also be calculated from equilibrium chemistry alone. Standard numerical codes which combine chemical equilibrium calculations with the gasdynamic C-J conditions are available for this purpose (5).

Detonation pressure ratios and velocities for some fuel-air mixtures at stoichiometric composition are given in Table I, and the variation of C-J detonation velocity, pressure ratio and temperature ratio with fuel-air composition are shown in Figures 1a), b) and c), respectively. The fuel-air composition is denoted by the equivalence ratio, which is defined as the fuel to air ratio divided by the fuel to air ratio at stoichiometric composition. Also included in Table I and plotted in Figure 1d, is the chemical energy, Q, released in the detonation wave. This parameter can be used to estimate the far-field blast wave from a detonating cloud by comparing with the blast from an equivalent energy TNT solid-explosive charge (6). The energy content of TNT is about 4.2 MJ/kg, which can be compared with 2.0 MJ/kg of mixture for a stoichiometric H_2S/air cloud. Since stoichiometric H_2S/air contains only 8% H_2S by mass, this corresponds to 22 MJ/kg of H_2S. It must be emphasized that blast estimates based on TNT equivalent energy are reliable only in the far-field and should not be used for locations close to the fuel-air cloud (i.e., closer than twice the maximum dimension of the cloud).

2.2 Minimum Initiation Energy

A minimum quantity of energy is required in order to establish a detonation in a given explosive mixture. This energy depends on the geometry of the cloud, the boundary conditions and the source of the energy. For fuel-air mixtures, the critical initiation energy is usually characterized by the minimum mass of tetryl high-explosive required to initiate a spherical detonation in an unconfined cloud. The equivalent energy of tetryl is approximately 4.2 KJ/kg. The minimum tetryl initiation masses for several fuel-air mixtures are given in Table I. These range from about 1 g for acetylene and hydrogen to an estimated 22 kg for methane. Further data, including data for off stoichiometric compositions can be found in the reviews by Bull (11) and by Lee (12). The dependence of the critical energy on composition is typically in the form of a U-shaped curve with the minimum near stoichiometric composition. Matsui and Lee (13) proposed that this minimum energy be used as a relative measure of the detonation hazard of the gas mixture.

Unfortunately, the critical initiation energy is relatively difficult to measure experimentally. It is usually determined by a GO NO-GO procedure based on the variation of high-explosive charge detonated in a cloud of the mixture. For insensitive fuel-air mixtures, 100 g or more of explosives are required to initate detonation and large clouds are necessary to ensure that a stable detonation has been established. Furthermore, the explosive charges must be carefully prepared and positioned away from cloud boundaries in order to ensure consistent results. Due to these experimental difficulties, critical tube diameter tests have to a large extent replaced critical energy tests for determining the detonation sensitivity of fuel-air mixtures.

2.3 Critical Tube Diameter

The critical tube diameter, d_c, is the minimum diameter of a round tube for which a detonation wave emerging from the tube will successfully re-establish itself in a surrounding unconfined cloud. With a smaller tube and the same explosive mixture, the expansion as the detonation wave diffracts from the tube causes the shock wave and combustion zone to separate to such an extent that the detonation is quenched. The critical tube diameter is therefore a measure of the minimum frontal size of detonation required for stable propagation in an unconfined cloud. In other words, an unconfined cloud with one dimension less than d_c could not support a detonation.

The critical tube diameter is as characteristic of an explosive mixture as the critical initiation energy and provides an alternative measure of detonation sensitivity. Based on a simple work-done model, Matsui and Lee (13) obtain a relationship between these two detonation parameters of the form, $E_c \propto d_c^3$. Although such a relationship provides a reasonable correlation for many fuels, the proportionality factor depends on the fuel (14).

Critical tube diameters for some common fuel-air mixtures at stoichiometric composition are included in Table I. Notice that these mixtures span a large range of critical tube diameters, from a minimum of 0.115 m for acetylene-air up to an estimated value of about 3.6 m for methane-air. These data, as well as data for off-stoichiometric compositions are summarized in References 12 and 14. The variation with composition is again represented by a U-shaped curve with a minimum critical tube diameter, corresponding to maximum sensitivity, near stoichiometric composition.

Both the critical tube diameter and the critical initiation energy are intimately related to the cellular detonation structure and the detailed chemical kinetic processes within the cellular detonation front. In fact, empirical relations between these parameters and the parameters which characterize the detonation structure have been established. These relations are now being used to determine the detonation sensitivity of an explosive mixture based solely on the scale of the detonation structure.

2.4 Detonation Structure

A detonation wave consists of a three-dimensional shock structure which includes transverse waves moving perpendicular to the detonation front as illustrated in Figure 2a (10, 15). A "footprint" of this structure can be recorded by placing a soot-coated foil parallel to the direction of propagation. As the detonation passes the soot-foil, the slipstreams behind the triple-point shock interactions trace out a diamond shape structure as seen in Figure 2b. It is the width of the diamonds in this structure, corresponding to the maximum separation of the transverse waves, which is measured as indicated in Figure 2c (16). The cell width, S, is also commonly referred to as the detonation cell size or cell diameter. The cell length is approximately 1.6 times the cell width (17).

The detonation cell size is another fundamental length scale which can be used to characterize the sensitivity of an explosive mixture, with larger cells corresponding to less sensitive mixtures. For a given mixture, the cell is usually smallest close to stoichiometric composition and increases in size away from stoichiometry as the mixture becomes less sensitive. The cell sizes for some common fuel-air mixtures at stoichiometric composition are included in Table I (12, 14, 16 – 18).

The regularity of the cellular structure depends on the explosive mixture. For less sensitive mixtures with large cells, the structure can become highly irregular with many modes of cellular patterns. Identification of the dominant mode is therefore subject to some interpretation (14). There is now considerable experimental evidence that the cell size, properly interpreted, is related to the critical tube diameter through the simple relation, $d_c = 13\ S$ (12, 18, 19). For the fuel-air mixtures included in Table I, the ratios of critical tube diameter to cell size are between 11.7 (for acetylene) and 15.4 (for ethylene), in good agreement with the empirical $d_c = 13\ S$ relation. The sensitivity of an explosive mixture can therefore be determined by simply monitoring the structure of detonations in the mixture. This method is now widely used, particularly for the less sensitive fuel-air mixtures and for other systems which are not amenable to large scale critical tube diameter testing. Cell size measurements are being used, for example, to determine the detonation sensitivity of hydrogen/air/steam at elevated temperatures for nuclear reactor safety studies (20, 21).

The modelling of the coupled chemical kinetic-gasdynamic processes within a cellular detonation front is still in the early development stages (22, 23), so that predictions of the cell size for a given mixture cannot yet be made in a reliable manner. However, comprehensive chemical kinetic models have been used to calculate the one-dimensional ZND induction zone length, Δ. It is then assumed that the cell size is proportional to this length (i.e., $S = A\Delta$). Based on this assumption, extensive induction length calculations have been performed by Westbrook (24 – 26) in order to predict cell sizes for various hydrocarbon and hydrogen systems. Roller and Shepherd (27) have also used this approach to predict the detonability of hydrogen/air/steam and hydrogen/air/carbon dioxide mixtures. In general, agreement with experiments is good, although deviations from a linear relationship are observed, particularly for very lean and rich mixture compositions. Furthermore, the proportionality factor, A, depends on the fuel-air system so that some cell size and/or critical tube diameter data are required to determine this factor.

2.5 Detonability Limits

From the practical point of view it is important to know for what fuel-air compositions a mixture is detonable. For an unconfined cloud, the minimum dimension of the cloud must be larger than the critical tube diameter in order for the cloud to support a detonation. Detonability limits could therefore be defined based on the size of the cloud. This does not take into account the energy required to establish a detonation in the cloud. For large unconfined clouds, composition limits based on initiation energy are probably more meaningful than those based on cloud size. In other words, the compositional limits are determined by specifying the maximum amount of energy or mass of solid explosive available to initiate a detonation. Mixtures which require less energy than this specified maximum are called detonable and those which require more are called non-detonable. The compositional limits therefore depend on the specified maximum energy (12)

Composition limits based on a specified maximum energy become meaningless in a realistic accidental spill scenerio where there are obstacles and partially confined spaces to accelerate the flame and cause localized explosions. In such situations the energy required to establish a detonation can be supplied by combustion of the mixture itself and need not be supplied externally. Recent studies of transition to detonation show that explosions of pockets with dimensions of the order of the critical tube diameter can cause onset of detonation in a surrounding cloud (4). This is not the only possible mechanism for transition to detonation, but all mechanisms do rely on achieving fast enough combustion to produce shock waves of sufficient strength and duration to cause onset of detonation (3). Reliable criteria for transition to detonation in terms of minimum flame speed, rate of burning and energy release are not yet available. Such criteria will depend on the reaction chemistry which is characterized, at least globally, by the detonability parameters previously described.

The critical tube diameter, or equivalently the cell size, also determines the size of opening required for a confined detonation to transmit into a surrounding cloud. Since transition to detonation is much more likely in confined spaces, such transmissions can be important for explosion hazards evaluation.

Specifications of detonability limits for realistic accidental spill scenerios must therefore take into account not only the initial conditions (i.e., the ignition source) but also the boundary conditions (i.e., the presence of obstacles and partial confinement). For accidental spill situations, it is therefore more meaningful to base limits on the dimensions of the cloud in relation to the critical tube diameter. If these dimensions are smaller than the critical tube diameter, the unconfined parts of the cloud cannot support a detonation. Even in highly confined geometries, a minimum size of cloud is required in order for a stable detonation to propagate. The limiting condition in a confined tube, for example, occurs when only one transverse wave is present. This mode of propagation is called "single-head spin" propagation (9, 15).

The cell size at the onset of single-head spin in a tube of diameter D can be calculated by assuming a purely acoustic transverse wave. This gives a spin pitch (or cell length) to tube diameter ratio, $P/D = \pi V/k_1 c$, where V is the detonation velocity, c is the local speed of sound and k_1 is the first root of the derivative of the Bessel function of order one ($k_1 = 1.841$). The corresponding cell width is then given by, $S \cong 0.6\ P$. Moen *et al.* (9) used the onset of "single-head spin" in different diameter tubes to determine the cell size for several ethylene-air mixtures. The cell sizes obtained in this manner are in excellent agreement with those measured from soot foils.

From the above discussions, it is clear that there are many ways of characterizing the detonability of an explosive mixture. Fortunately, theoretical and empirical links have been established in recent years, so that the assessment of detonability can now be made in a reliable manner using a variety of methods. In the investigation of hydrogen sulphide/air mixtures, we have taken advantage of these links to minimize the number of tests required with this highly toxic material.

3. EXPERIMENTAL DETAILS

The experimental test series was performed at the DRES fuel-air facility. An aerial view of the facility showing the test pad, instrumentation and fuel-flow control trailers, and high-speed camera shelters is included as Figure 3a. The facility, which is described in detail in Reference 28, is centered around an 18.3 m × 7.6 m concrete test pad onto which the experimental apparatus can be mounted. A photograph of the test pad with a typical test section used in the present critical tube diameter tests is shown in Figure 3b. The test section consisted of a 0.89 m diameter steel tube, 7.8 m long, attached to either a 1.8 or 0.89 m diameter polyethylene bag at one end. The length of the bag was varied from 0.5 m to 5 m, depending on the test. A schematic diagram of a typical test configuration is shown in Figure 3c.

In addition to tests using hydrogen sulphide (H_2S), two tests were performed using butane (C_4H_{10}) as a fuel so that a direct comparison between detonations with H_2S and a common hydrocarbon fuel could be made. The test gases (Technical grade, 99% pure H_2S or CP grade, 99% pure C_4H_{10}) were mixed with the initial air in the test volume by a multipath recirculation system using a high-capacity centrifugal blower.

The composition and mixture homogenity in the test volume were monitored by continuously analyzing samples taken from two ports in the tube using a "Wilks Miran 1A" infrared gas analyzer. The absorption spectrum for hydrogen sulphide shows that this gas is a poor absorber in the infrared. A small absorbance peak can be found at wavelength, $\lambda = 3.70\ \mu m$, with other peaks between $\lambda \sim 7.5\ \mu m$ to $\lambda \sim 9.5\ \mu m$. The poor absorbtion characteristics of hydrogen sulphide required that large absorption pathlengths be used. This greatly increased the possibility of small impurities affecting the infrared readings. The concentration of H_2S during the first three trials were monitored at a wavelength of $8.0\ \mu m$. At this wavelength, impurities in the system tended to overestimate the hydrogen sulphide concentration. Subsequent trials were conducted using $\lambda = 3.70\ \mu m$. The difficulties in assuring an accurate mixture were then significantly reduced, and the maximum uncertainty in H_2S concentration was less than $\pm$ 0.25% H_2S. With butane as a fuel, this uncertainty was less than 0.05% C_4H_{10}.

Once the desired fuel-air composition had been attained in the test volume, detonation was initiated at the far end of the tube using a DM12 high-explosive charge. In one test, this charge was placed on the pad at the centre of the bag.

The arrival and pressure profile of the wave were monitored at various positions along the tube and bag using piezoelectric pressure transducers. Far-field pressure profiles were also monitored in selected tests. The positions of the pressure transducers is shown in Figure 4. High-speed photographic records of the transmission and propagation of the wave were obtained using a Photec camera ($\sim$ 12,000 half-frames/sec) placed 90° to the tube axis. A Hycam camera ($\sim$ 12,000 half-frames/sec) placed at a 30° angle, as well as an end camera ($\sim$ 12,000 frames/sec) looking directly down the tube, were also used on selected trials. The positions of these cameras are illustrated in Figure 4. The detonation cell structure was recorded by placing a large steel sheet (3 m long by 1.5 m wide) around the inside walls of the tube. This sheet was carefully sooted using a rich burning acetylene-oxygen torch.

Since hydrogen sulphide and the main product of combustion, sulphur dioxide, are both highly toxic, special safety procedures were followed in carrying out the tests. These procedures are outlined in Appendix A.

4. RESULTS AND DISCUSSION

A summary of the trials performed is given in Table II. For all hydrogen-sulphide/air mixtures, the detonation failed to transmit from the tube into the bag. The critical tube diameter for H_2S/air is therefore larger than 0.89 m. For butane/air mixtures, however, the detonation successfully transmitted into the bag so that for these mixtures the critical tube diameter is less than 0.89 m.

4.1 Equilibirum Detonation Properties

The failure of the detonations to re-establish themselves in the bag for H_2S/air mixtures was confirmed from both the high-speed photographic records and the pressure records. A typical set of pressure records showing failure in the bag is included in Figure 5. The records in the tube (Positions #1, 2, 3) are characteristic of a stable detonation wave propagating at a velocity of 1660 m/s with a peak overpressure of about 15 atmospheres. The pressure fluctuations observed during the first millisecond or so after the arrival of the wave are due to pressure variations within the three-dimensional detonation structure. As the detonation wave propagates into the bag, it is quenched by the expansion and fails to re-establish itself. By the time the pressure wave reaches Position #5, 3 m from the tube exit, the peak overpressure is less than 3 atmospheres.

As discussed in the previous section, H_2S concentrations measured by the IR analyzer in Trials #10, 11 and 12 were higher than actual due to the presence of impurities. The H_2S/air compositions were therefore inferred from the detonation velocity measured in the tube. Previous tests, in the same 0.89 m tube for a variety of fuel-air mixtures, show that the measured detonation velocities are in excellent agreement with the calculated C-J values. Typically, the observed velocity is 1 – 2% less than the calculated velocity. This observed velocity deficit is due to boundary effects in the tube. Based on these previous observations, the composition in Trials 10, 11 and 12 was inferred by taking one concentration limit at the C-J velocity corresponding to the observed velocity and the other limit at a C-J velocity 2.5% larger. The reliability of this estimate was confirmed in two subsequent tests (Trial #26 and 29) with more accurate IR-analyzer readings. The measured detonation velocities are tabulated in Table III, and the observed and calculated detonation velocities for H_2S/air are compared in Figure 6. For both Trial #26 and 29 the measured velocity is within 2.5%

of the calculated value. Detonation velocities observed in butane/air are also within 2.5% of the calculated C-J value. The compositions inferred for Trials # 10, 11 and 12, as indicated in Figure 6, should therefore give a reliable estimate of the H_2S/air mixture in the test section.

A further check on the composition and the stability of the detonation waves in the tube is provided by detonation pressure inferred from the pressure records. Unfortunately, these records can be difficult to interpret due to the pressure fluctuations. An estimate of the C-J pressure can be obtained by extrapolating a curve representing the average pressure over a 1 ms interval to the time of arrival. The results from such estimates are included in Table III. The pressures measured in H_2S/air mixtures are compared with the theoretical C-J pressures in Figure 7.

4.2 Cell Size and Critical Tube Diameter

The above comparisons between observed and calculated equilibrium detonation properties confirm that stable detonations in H_2S/air were established in the tube. None of these detonations successfully transmitted into the bag so that a direct measure of a critical tube diameter could not be made. Only a lower bound of 0.89 m on the critical tube diameter for H_2S/air could be established. A more quantitative assessment of the detonability was obtained from the cellular structure recorded on the sooted steel sheets. Cell structures observed for near stoichiometric butane/air and two H_2S/air mixtures are compared in Figure 8. This comparison shows that the cell size in stoichiometric H_2S/air is about twice that in stoichiometric C_4H_{10}/air. For mixtures with 10% H_2S, the cell size is more than a factor of two larger than at stoichiometric H_2S/air composition. The cell sizes measured in the present tests are given in Table III and cell structure records from all the H_2S air tests are included in Appendix B.

The two additonal cell size data for H_2S/air shown in Table III were obtained by re-examining pressure records from tests performed at McGill University in a 145 mm diameter tube (8). These records show that single-head spin appears in this tube for H_2S concentrations between 9% – 10% and 20% – 22%. Using the relation, $P/D = \pi V/k_1c$, discussed in Section 2.4, this gives a spin pitch or cell length of 432 mm between 9 – 10% H_2S and 440 mm between 20 – 22 % H_2S. The corresponding cell widths based on $S = 0.6\ P$ are 260 mm and 264 mm, respectively.

As discussed in Section 2.4, the one-dimensional ZND induction zone length, Δ, has been used as an alternate detonation sensitivity parameter. Induction zone length correlations have been relatively successful in describing the variation in detonation parameters with composition and additives for a variety of mixtures (24 – 27, 29). The predictions of Roller and Shepherd for the hydrogen/air/steam system are particularly impressive (27). At our request, Shepherd performed similar calculations for the H_2S/air system (30). His chemical-kinetic calculations are based on 51 reactions and 17 species, and he defines an induction length as the length from the shock to the location of the point at which the local gas velocity is 0.95 of the local speed of sound (Mach No. $M = 0.95$) in a one-dimensional ZND model of the detonation wave. This point occurs at a distance slightly after the point of maximum rate of temperature increase as illustrated in Figure 9. Shepherd's results for the induction zone length are plotted as a function of H_2S/air composition in Figure 10. A comparison of the variation of the cell size with that of the induction zone length can be made by assuming a linear relationship between these two length scales as discussed in Section 2.4. For H_2S/air, the scaling factor relating the cell size and the induction zone length was determined by normalizing to a cell size of 110 mm at 14.2% H_2S. This gives a scaling factor of 17.8, which can be compared with a factor of 24.2 obtained for hydrogen/air mixtures. The comparison of measured cell size with scaled induction zone length in Figure 11, shows that this correlation is in good agreement with experiment and that the scaled induction zone length can be used to predict cell sizes for H_2S/air compositions between about 9% and 22% H_2S. Extrapolation to leaner and richer mixtures is also possible. However, previous results for other fuel-air mixtures show that such extrapolations tend to underestimate the sensitivity of very lean and rich mixtures(14, 16).

The empirical correlation $d_c = 13\ S$ can now be used to estimate the critical tube diameter for comparison with more common fuels. Critical tube diameters for a variety of fuel-air mixtures are compared with those for H_2S/air in Figure 12. The results for acetylene, hydrogen, ethylene and propane are based on the correlations of critical tube diameter results by Moen *et al.* (14). All the other results are based on a 13 S estimate. The minimum critical tube diameter for H_2S/air is 1.3 m at stoichiometric composition. This can be compared with minimum critical tube diameters less than 0.9 m for common fuels such as propane and butane. Only methane/air mixtures are less sensitive to detonation with an estimated minimum critical tube diameter of almost 4 m.

4.3 Minimum Initiation Energy

A good illustration that the energy required to initiate a detonation depends on the configuration of the cloud and the cloud boundaries is obtained by comparing Trials # 10 and # 30. In both trials the mixture was about 10% H_2S in air. In Trial # 10, a 300 g explosive charge placed at one end of the tube successfully initiated an essentially planar confined detonation in the tube. However, in Trial # 30, a 500 g charge placed on the ground under the plastic bag failed to initiate an expanding hemispherical detonation in the bag. Furthermore, the 500 g charge was placed on a solid surface so that the effective energy of the charge is approximately doubled. Considerably more energy is therefore required to initiate a detonation in an unconfined cloud than in the same mixture confined in a tube.

The failure of an equivalent 1 kg mass of solid explosive to initiate an unconfined detonation in a 10% H_2S/air mixture, with an estimated critical tube diameter of 3.6 m, is consistent with the approximate $E_c \propto d_c^3$ relationship observed for other fuel-air mixtures. As shown in Figure 13, the proportionality factor depends on the mixture, but even using the factor for ethane fuel, which has the smallest factor, a minimum solid explosive mass of about 2 kg would be required to initiate a detonation in a H_2S/air mixture with the same critical tube diameter. It can therefore be concluded that the factor relating E_c and d_c^3 is not significantly smaller for H_2S/air mixtures. In other words, the minimum initiation energies estimated from Figure 13, based on the ethane curve, provides a lower bound to the energy required. For stoichiometric H_2S/air with a critical tube diameter of 1.3 m, this lower bound is 80 g of tetryl. However, as discussed above, this is for a completely unconfined cloud. The minimum energy could be significantly lower for confined clouds.

5. CONCLUSION

The relative detonation sensitivity of hydrogen sulphide/air mixtures has been determined in a series of large scale experimental tests. These tests show that H_2S/air mixtures are less sensitive to detonation than propane or butane/air mixtures. Evaluations based on these common hydrocarbon fuels therefore provide a conservative estimate of the detonation hazards associated with a spill of hydrogen sulphide.

A minimum critical tube diameter of 1.3 m is obtained for stoichiometric H_2S/air mixtures. This can be compared with corresponding critical tube diameters less than 0.9 m for both propane and butane/air mixtures. Of the common hydrocarbon gases, only methane forms a less detonation sensitive mixture than hydrogen sulphide when mixed with air.

The minimum energy required to establish a detonation in an unconfined hydrogen sulphide/air cloud, is estimated to be larger than that from 80 g of solid explosives. It is therefore unlikely that detonation could accidentally occur in such a cloud. However, most accidental spills occur in environments with obstacles and partially confined spaces. In such environments, flame acceleration and localized explosions will play an important role in assessing the detonation hazards. Although considerations of transition to detonation in such situations are outside the scope of the present investigation, it can be concluded that transition to detonation is less likely with hydrogen sulphide than with most common gaseous hydrocarbon fuels except methane.

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Table I

DETONATION PARAMETERS FOR FUEL-AIR MIXTURES

(Stoichiometric Composition; Initial Pressure 1 atm; Initial Temperature 298.15 K)

FUEL	% FUEL BY VOLUME	DETONATION PRESSURE RATIO	VELOCITY (m/s)	ENERGY RELEASE (MJ/kg mixture)	INITIATION ENERGY (g tetryl)	CRITICAL TUBE Diameter (m)	CELL WIDTH (mm)
Acetylene (C_2H_2)	7.75	19.1	1864	2.44	1.25	0.115	9.8
Hydrogen (H_2)	29.6	15.6	1968	2.82	1.1	0.20	15
Ethylene (C_2H_4)	6.54	18.4	1822	2.35	10 NO GO 15 GO	0.43	28
Ethane (C_2H_6)	5.66	18.0	1825	2.31	30 NO GO 40 GO	~ 0.9	54 – 62
Propylene (C_3H_6)	4.46	18.5	1809	2.31	12.5	0.7	—
Propane (C_3H_8)	4.03	18.3	1798	2.29	50 NO GO 80 GO	0.9	69
n-Butane (C_4H_{10})	3.13	18.4	1796	2.28	50 NO GO 80 GO	~ 0.7 (13 S)	50 – 62
Methane (CH_4)	9.48	17.2	1801	2.31	22×10^3 (estimate)	3.6 (13 S)	280 ± 30
Hydrogen Sulphide (H_2S)	12.3	15.3	1647	1.96	$\geqslant 80$	1.3 (13 S)	100
Hexane (C_6H_{14})	Aerosol	18.6	1795	2.28	25	—	—

Table II

FIELD TRIALS SUMMARY

TRIAL #	FUEL % (Bag Diameter × Length)	TOTAL GAS VOLUME DIAGNOSTICS	INITIATION CHARGE	COMMENTS
10	H_2S 9.6% – 10.3% (1.8 m × 3.0 m)	12.5 m³ Gas Mixture 6 Pressure Tranducers 1 Camera (90°)	300 g DM12	● Detonation failure in bag ● Obtained cell structure record
11	H_2S 10.5% – 11.4% (1.8 m × 3.0 m)	12.5 m³ Gas Mixture 6 Pressure Transducers 1 Camera (90°)	500 g DM12	● Detonation failure in bag ● Obtained cell structure record
12	H_2S 12.0% – 13.2% (1.8 m × 3.0 m)	12.5 m³ Gas Mixture 6 Pressure Tranducers 1 Camera (90°)	500 g DM12	● Detonation failure in bag ● Obtained cell structure record
26	H_2S 13.9% – 14.5% (0.9 m × 0.5 m)	5.2 m³ Gas Mixture 4 Pressure Transducers 1 Camera (0°)	300 g DM12	● Detonation failure in bag ● Obtained cell structure record
27	C_4H_{10} 3.1% – 3.2% (1.8 m × 3.1 m)	12.5 m³ Gas Mixture 4 Pressure Tranducers 3 Cameras (0° – 30° – 90°)	300 g DM12	● Successful detonation transmission into bag ● Obtained cell structure record
28	C_4H_{10} 3.1% – 3.2% (2.0 m × 4.8 m)	19.4 m³ Gas Mixture 6 Pressure Transducers 3 Cameras (0° – 30° – 90°)	300 g DM12	● Successful detonation transmission into bag ● Obtained cell structure record ● Far-field pressure results
29	H_2S 12.4% – 12.8% (0.9 m × 5.0 m)	8.0 m³ Gas Mixture 6 Pressure Tranducers 3 Cameras (0° – 30° – 90°)	300 g DM12	● Detonation failure in bag ● Obtained cell structure record ● Far-field pressure results
30	H_2S 9.5% – 10.0% (2.0 m × 4.8 m)	19.4 m³ Gas Mixture 6 Pressure Transducers 3 Cameras (0° – 30° – 90°)	500 g DM12 Placed on ground at centre of bag	● Charge failed to initiate detonation

Table III

MEASURED DETONATION PARAMETERS

TEST #	% FUEL (By Volume)	AVERAGE VELOCITY (m/s) (In Tube)	AVERAGE OVERPRESSURE (atm) (Three Readings)	CELL SIZE (mm)
10	9.6 – 10.3% H_2S	1544	13.6	265 – 290
11	10.5 – 11.4% H_2S	1587	14.3	160 – 190
12	12.0 – 13.2% H_2S	1660	15.2	100 – 130
26	13.9 – 14.5% H_2S	1633	14.8	102 – 118
27	3.1 – 3.2% C_4H_{10}	1817	16.2	50 – 60
28	3.1 – 3.2% C_4H_{10}	1784	15.6	55 – 62
29	12.4 – 12.8% H_2S	1611	15.2	85 – 120
Onset of single-head spin in 145 mm tube (McGill) Ref. 8	9 – 10% H_2S 20 – 22% H_2S	— —	— —	260 mm 264 mm

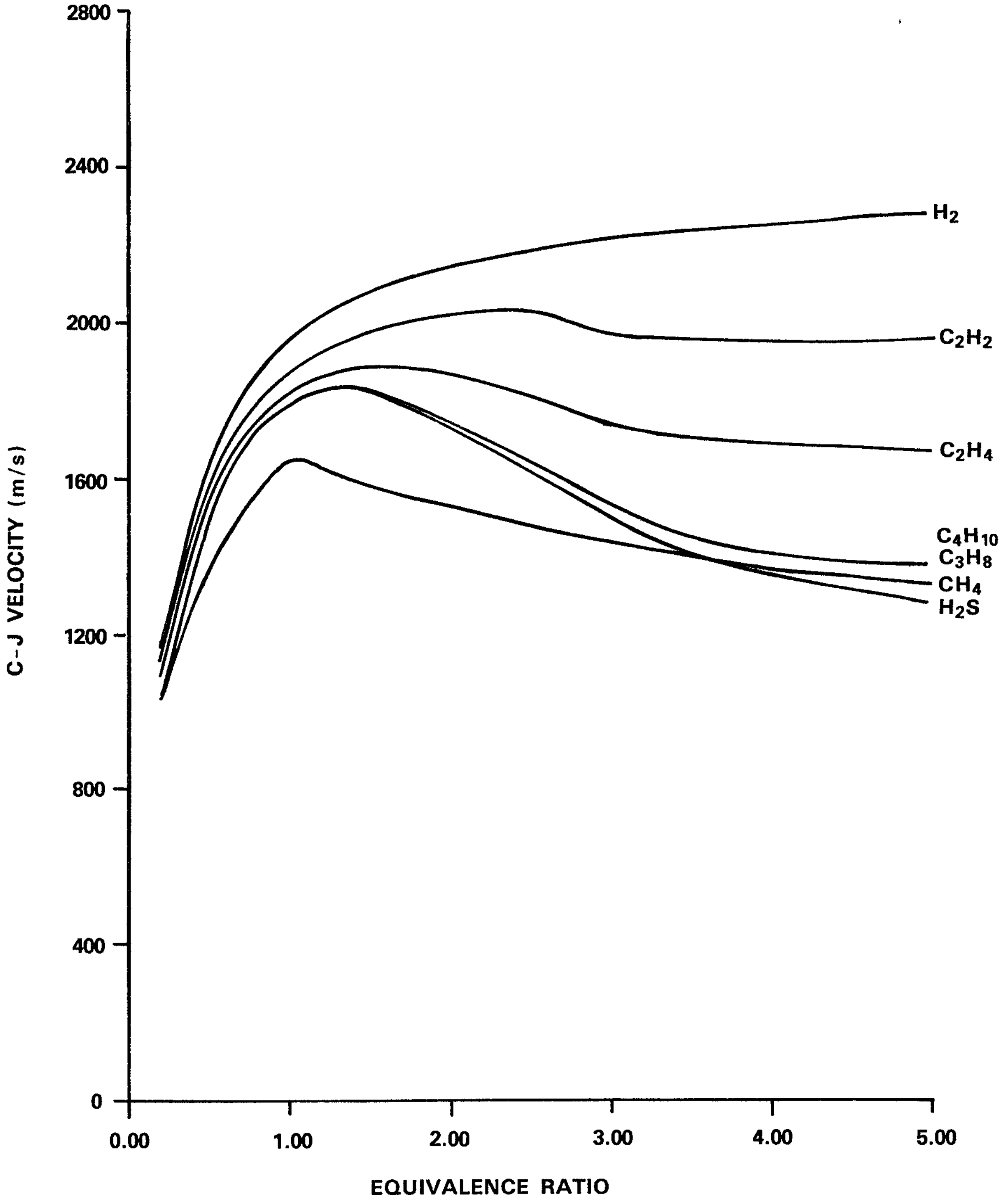

2800
2400
2000
1600
1200
800
400
0
C–J VELOCITY (m/s)
0.00
1.00
2.00
3.00
4.00
5.00
EQUIVALENCE RATIO
H_2
C_2H_2
C_2H_4
C_4H_{10}
C_3H_8
CH_4
H_2S

FIGURE 1a

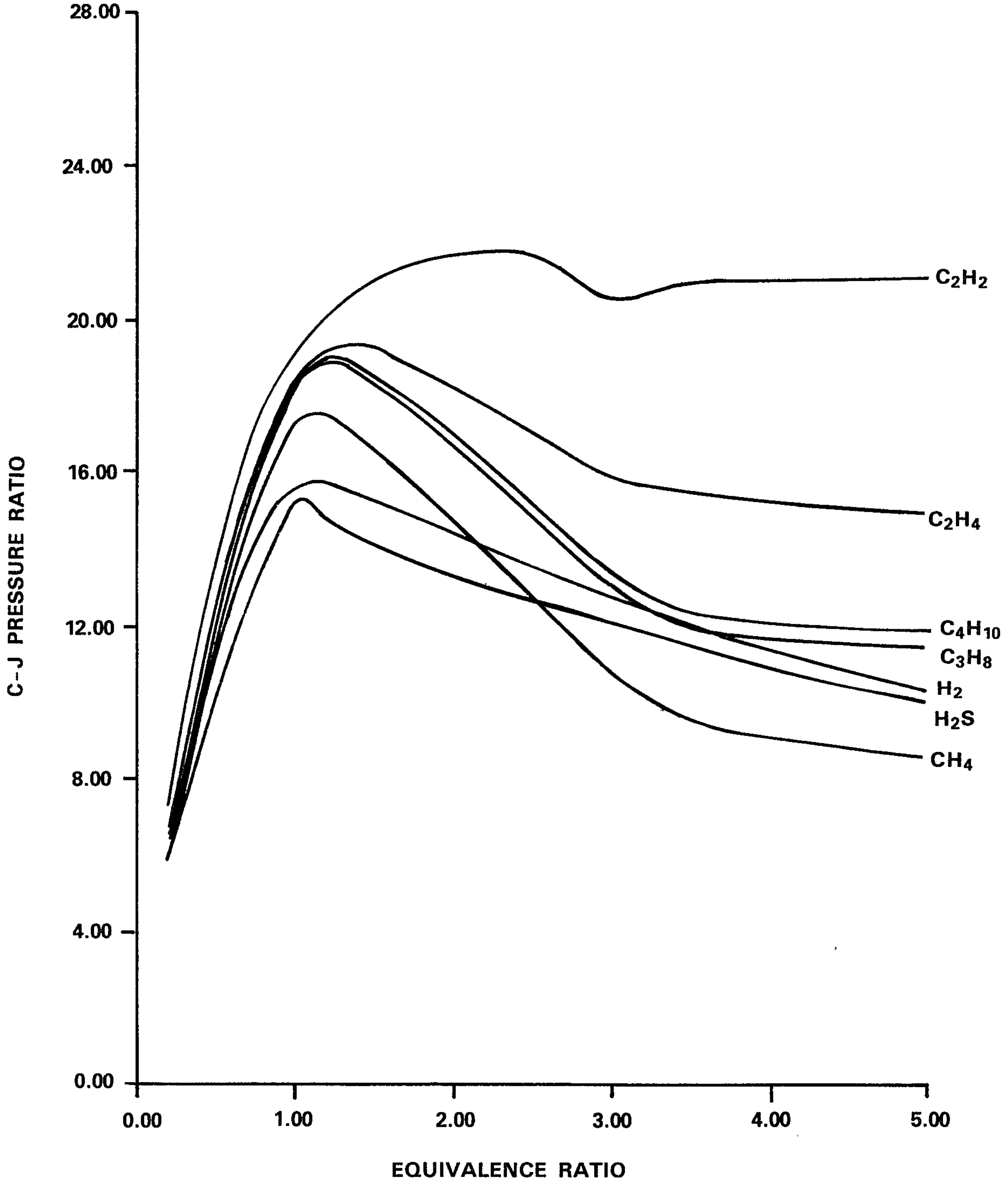

28.00
24.00
20.00
16.00
12.00
8.00
4.00
0.00
C–J PRESSURE RATIO
0.00
1.00
2.00
3.00
4.00
5.00
EQUIVALENCE RATIO
C_2H_2
C_2H_4
C_4H_{10}
C_3H_8
H_2
H_2S
CH_4

FIGURE 1b

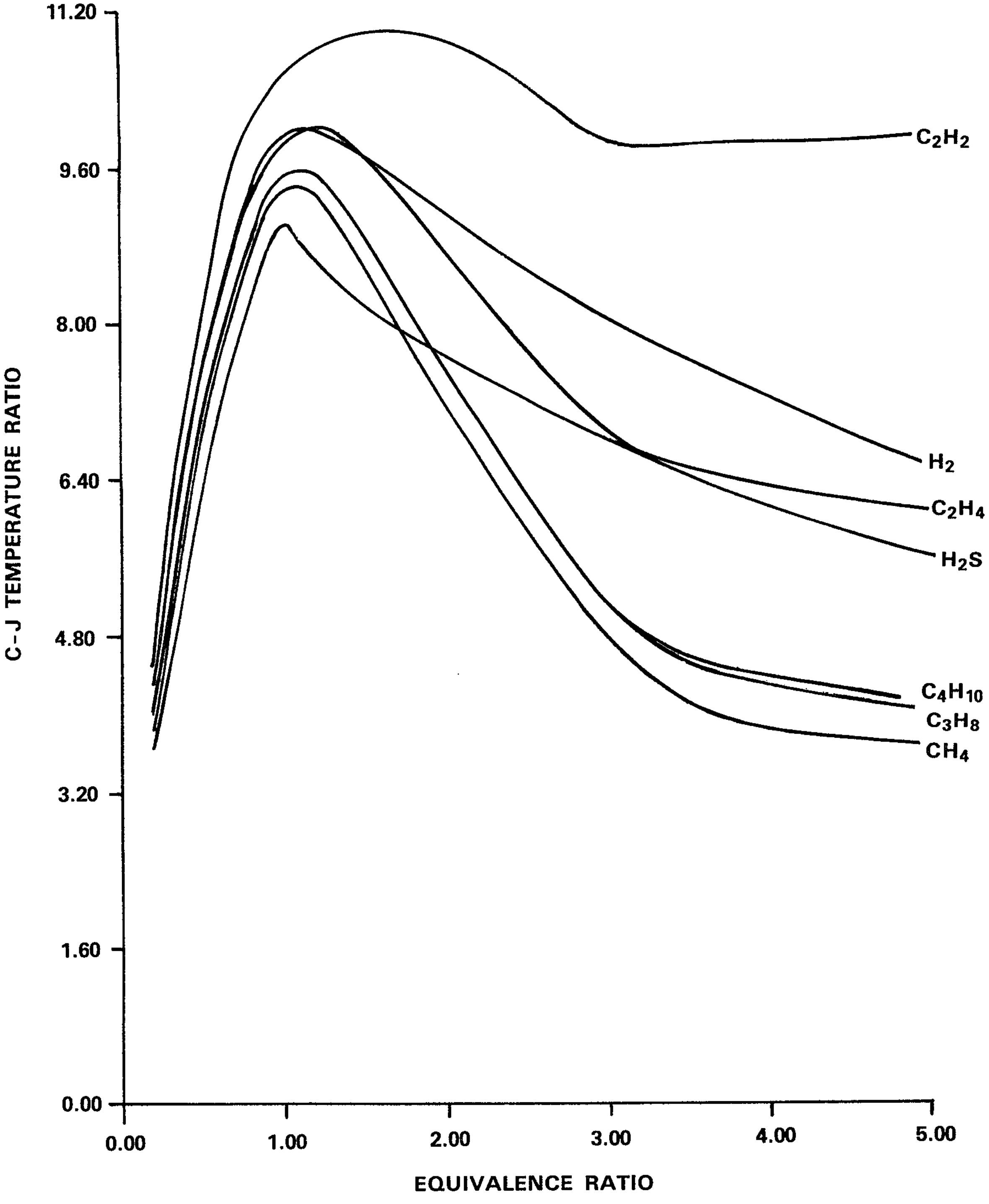

11.20
9.60
8.00
6.40
4.80
3.20
1.60
0.00
C-J TEMPERATURE RATIO
0.00
1.00
2.00
3.00
4.00
5.00
EQUIVALENCE RATIO
C_2H_2
H_2
C_2H_4
H_2S
C_4H_{10}
C_3H_8
CH_4

FIGURE 1c

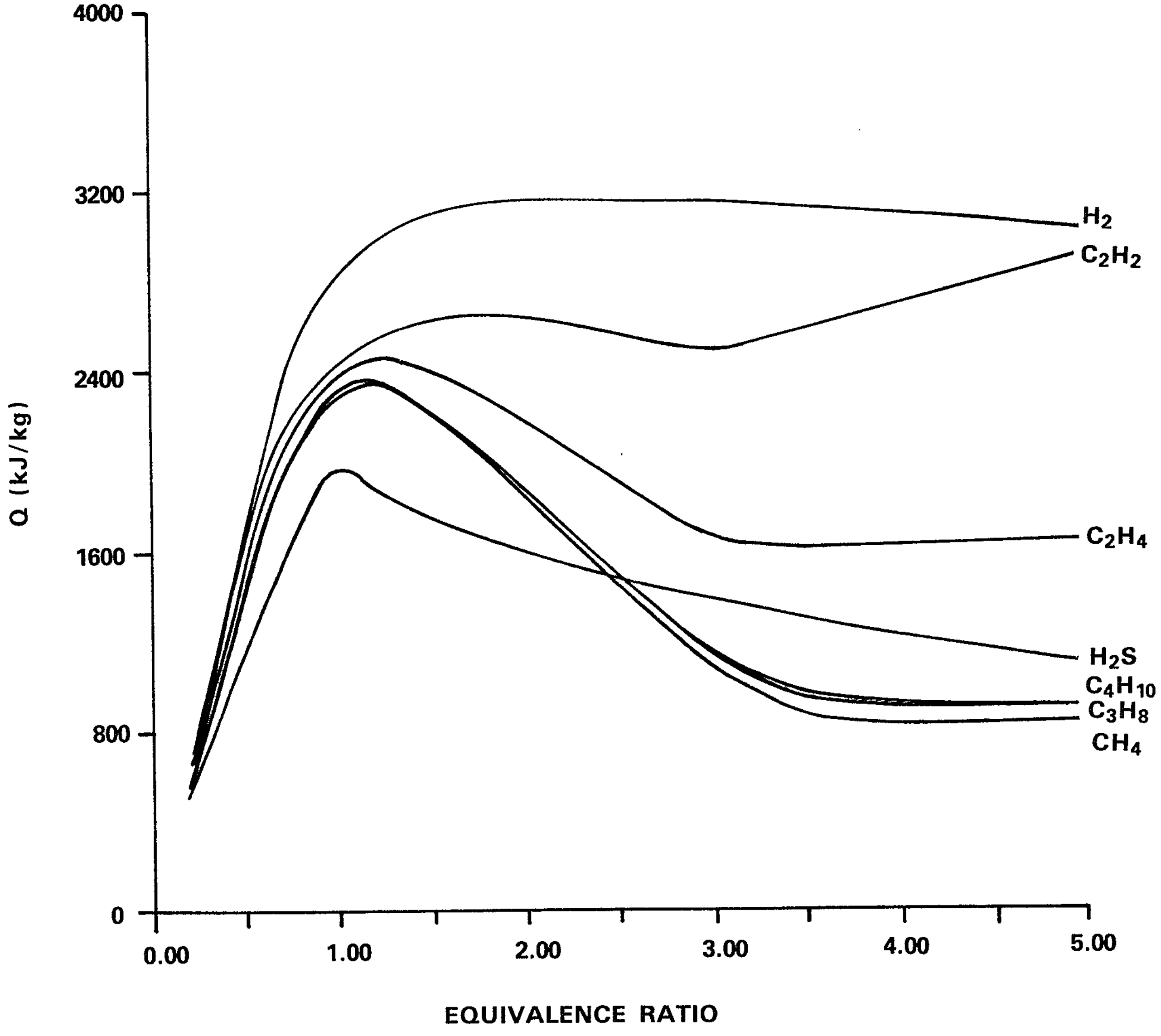
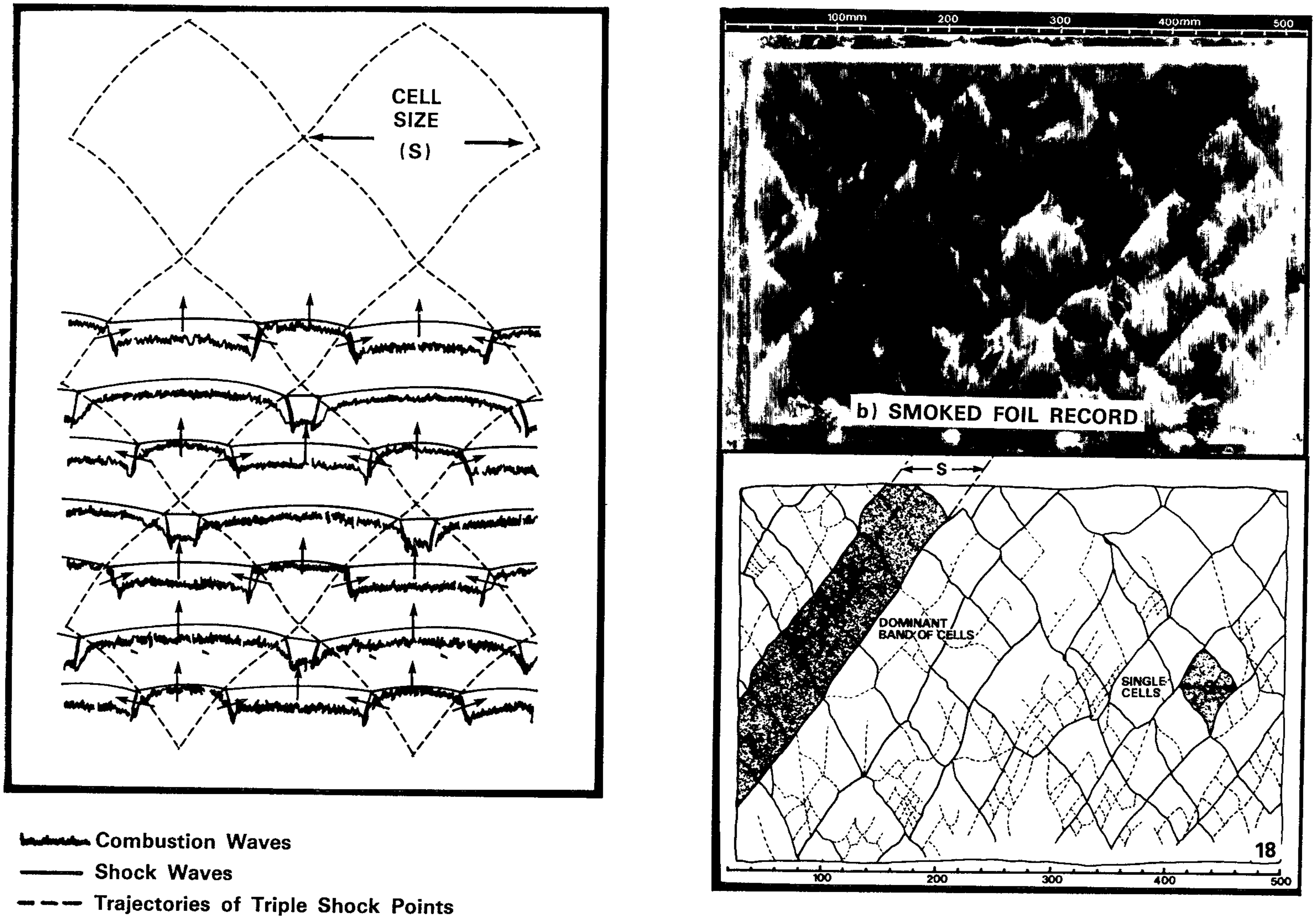

4000
3200
2400
1600
800
0
Q (kJ/kg)
0.00
1.00
2.00
3.00
4.00
5.00
EQUIVALENCE RATIO
H_2
C_2H_2
C_2H_4
H_2S
C_4H_{10}
C_3H_8
CH_4

FIGURE 1d



a) TRANSVERSE WAVE STRUCTURE OF GASEOUS DETONATIONS

c) INTERPRETATION OF SMOKED FOIL RECORD

Figure 2. TYPICAL CELLULAR STRUCTURE OF DETONATIONS IN FUEL-AIR MIXTURES

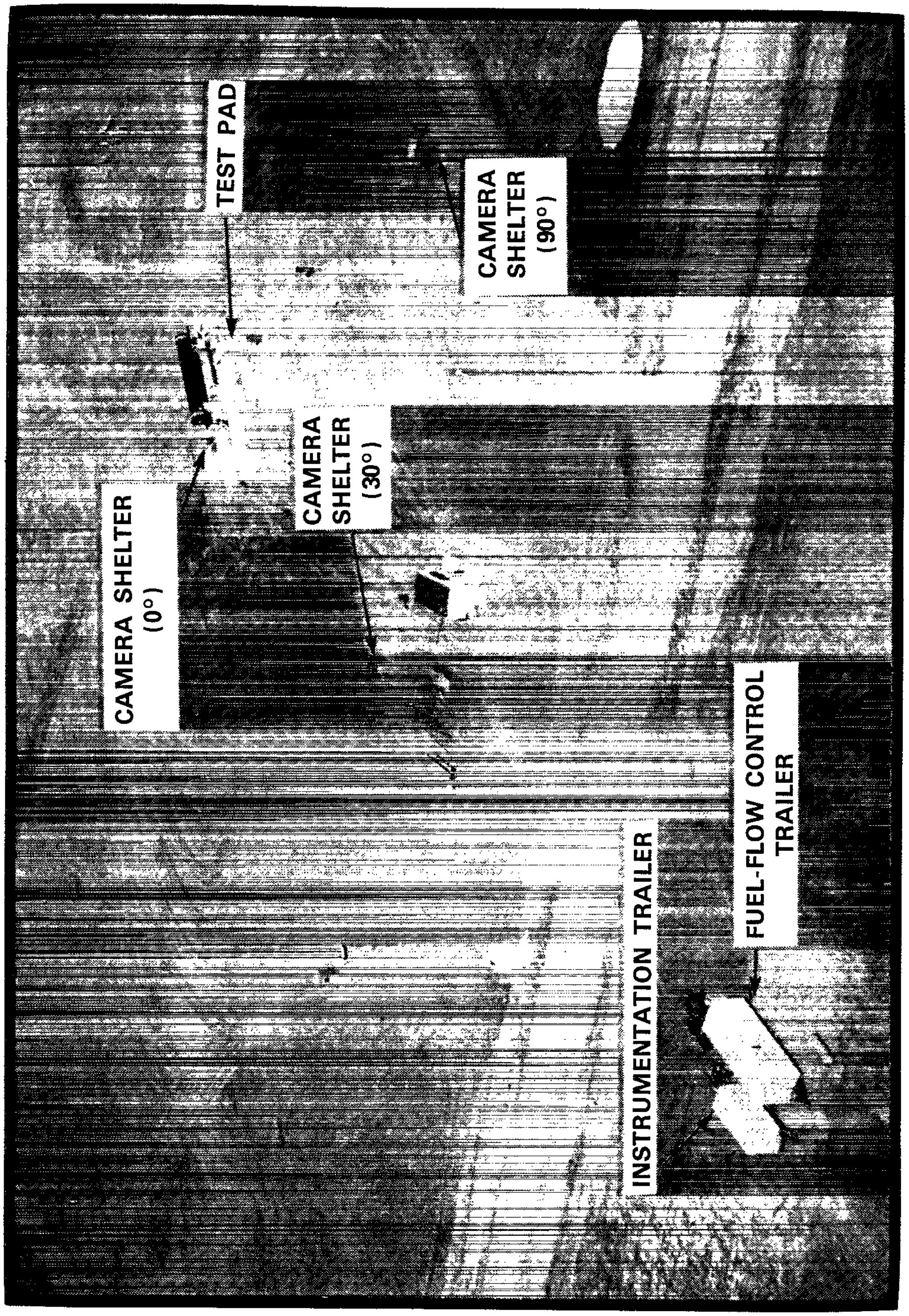


Figure 3a. AERIAL VIEW OF TEST SITE

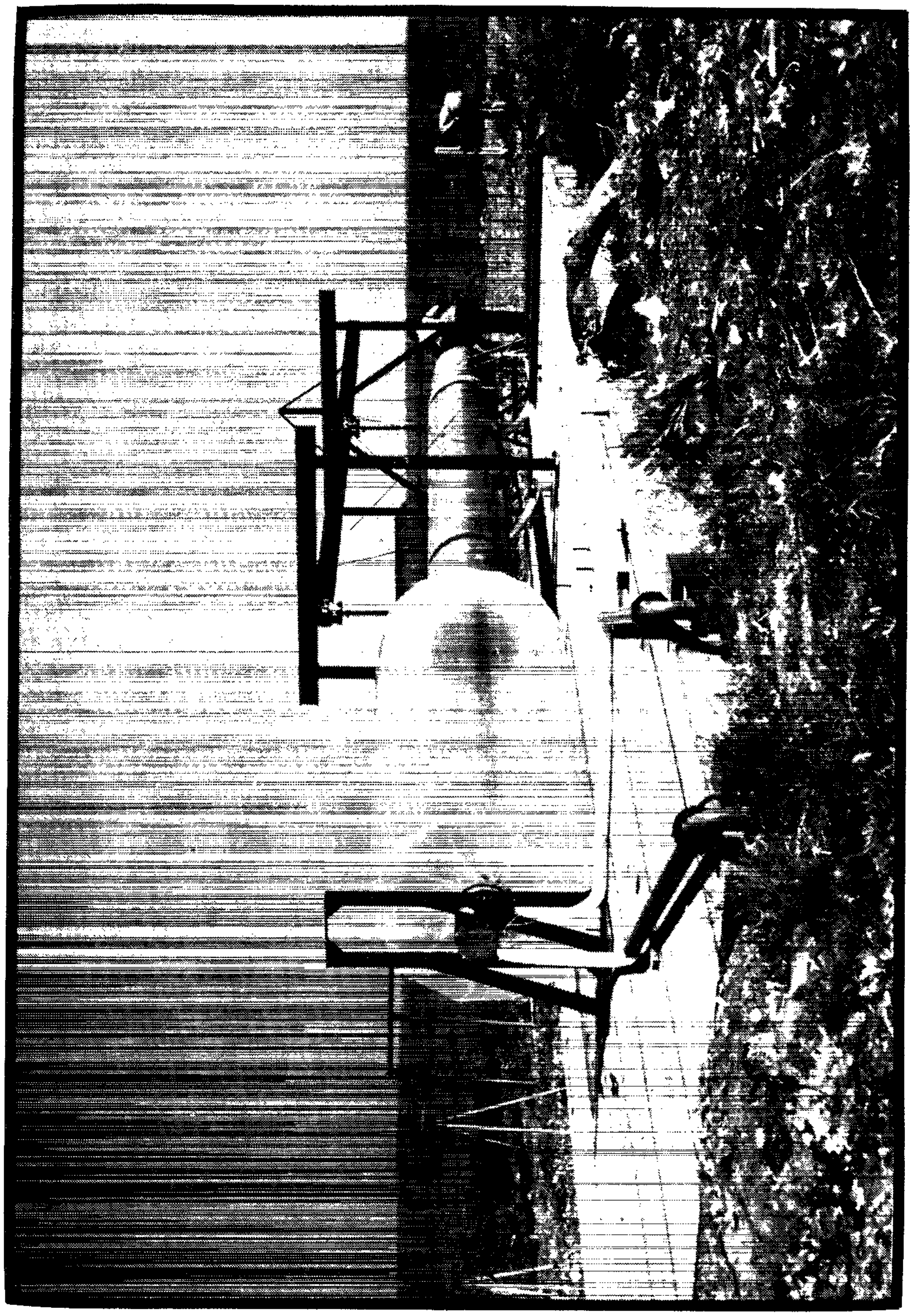


Figure 3b. EXPERIMENTAL LAYOUT

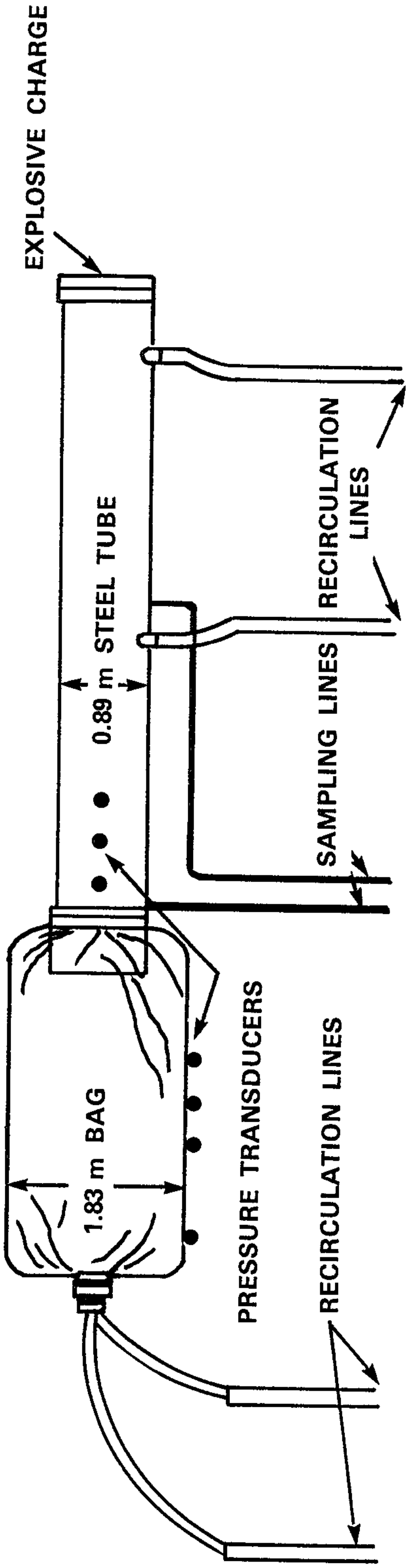
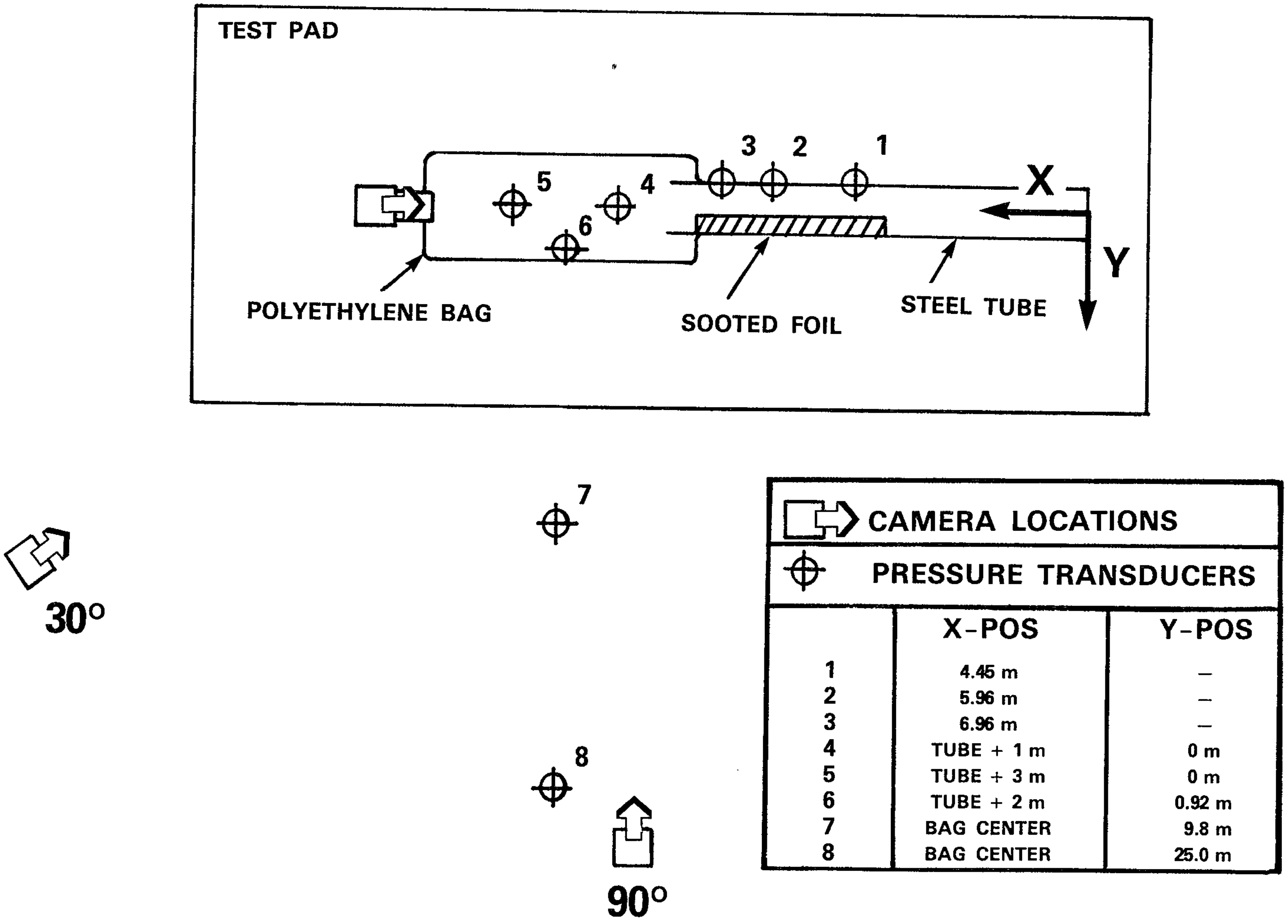


Figure 3c. SCHEMATIC OF EXPERIMENTAL LAYOUT



	X-POS	Y-POS
1	4.45 m	–
2	5.96 m	–
3	6.96 m	–
4	TUBE + 1 m	0 m
5	TUBE + 3 m	0 m
6	TUBE + 2 m	0.92 m
7	BAG CENTER	9.8 m
8	BAG CENTER	25.0 m

Figure 4. H_2S TRIALS: INSTRUMENTATION LAYOUT

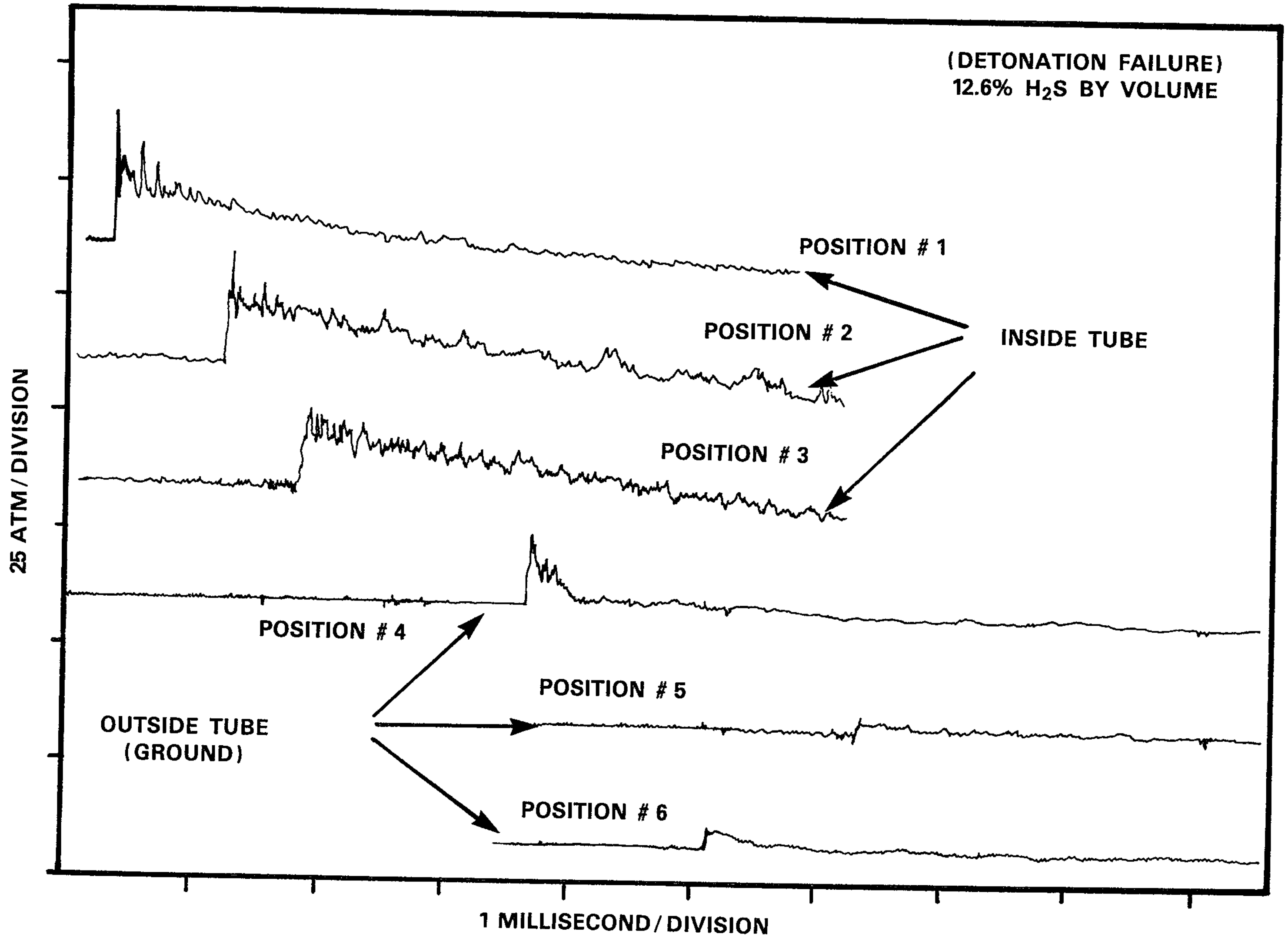


Figure 5. CRITICAL TUBE PRESSURE RECORDS

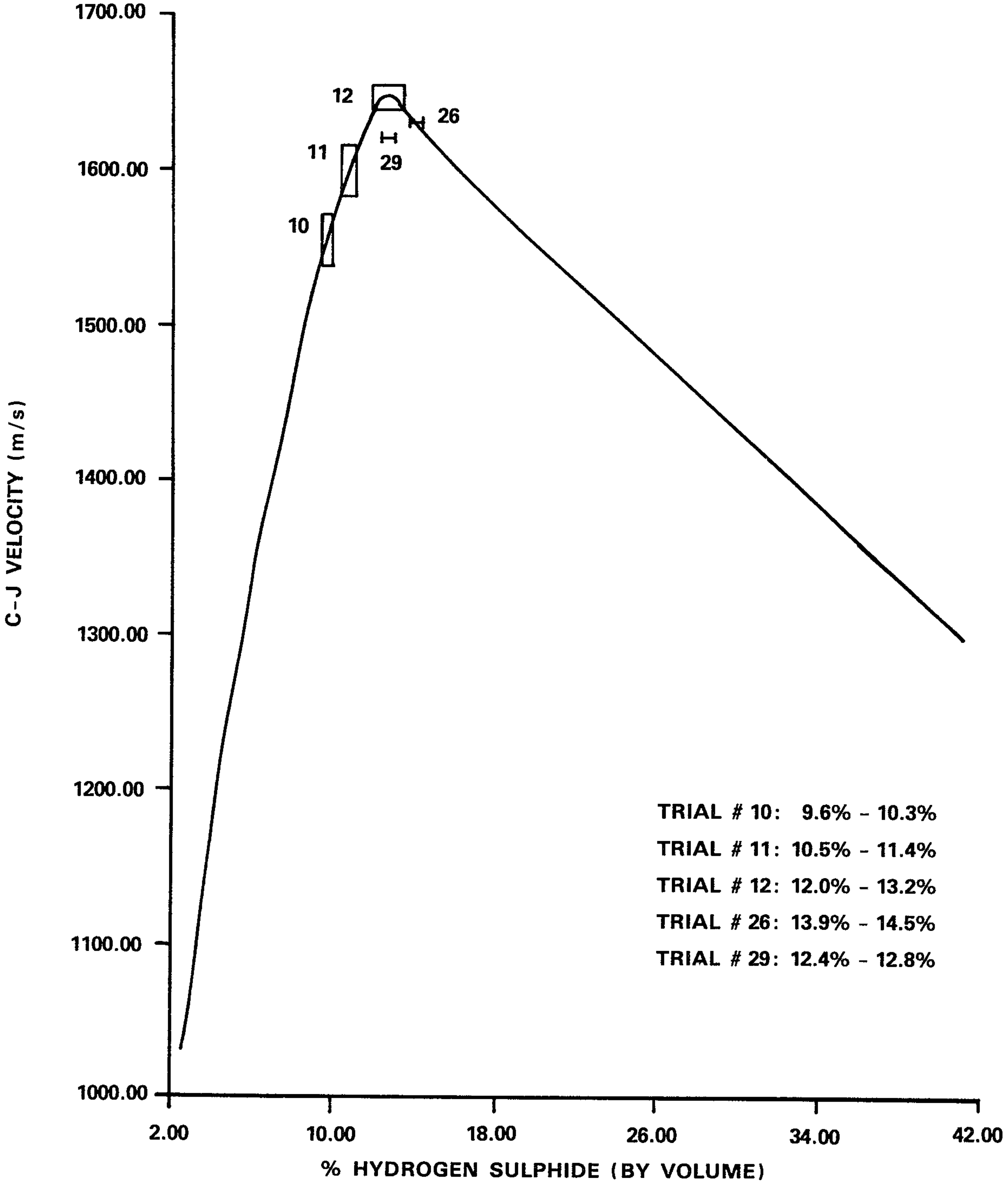


Figure 6. HYDROGEN SULPHIDE

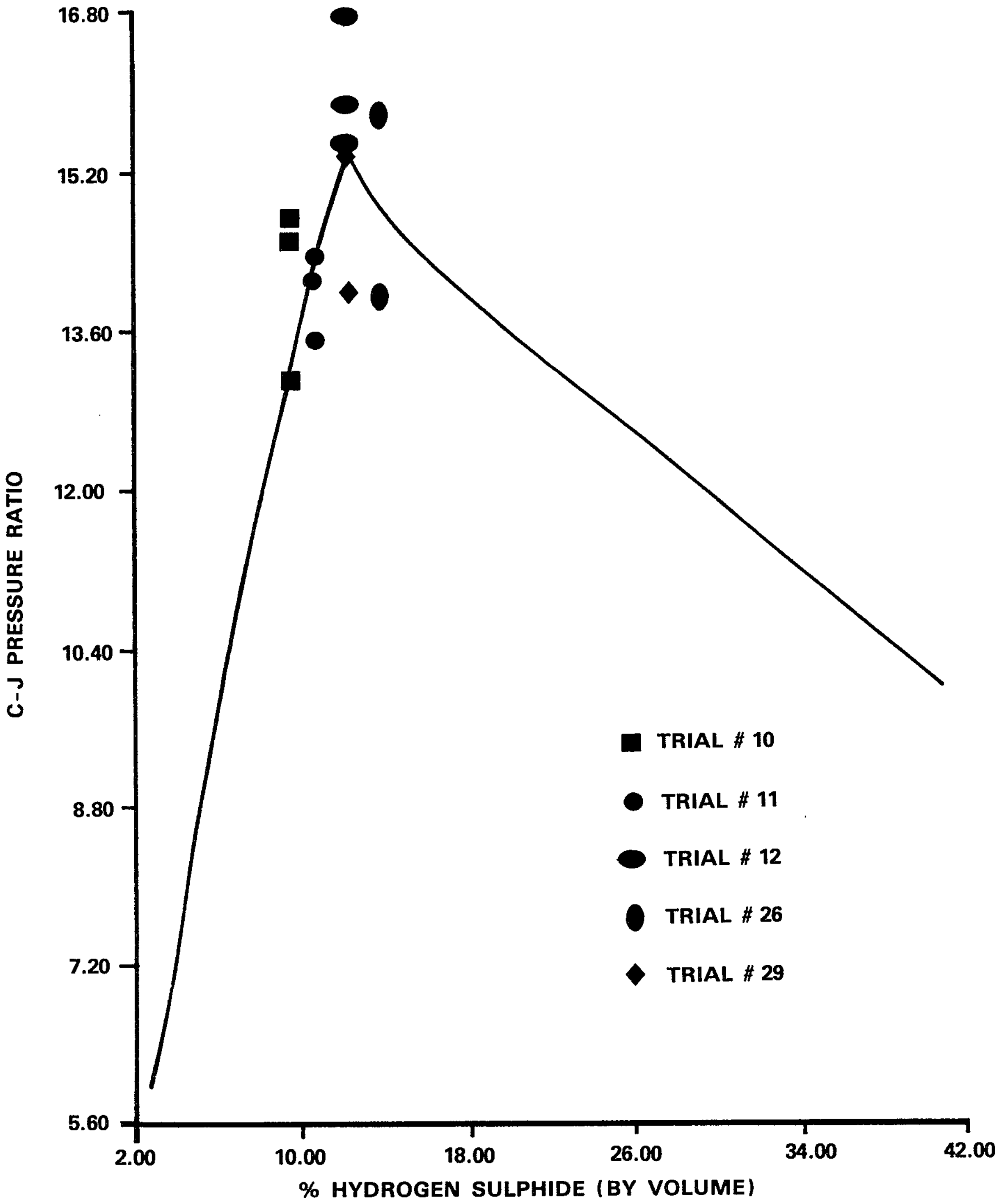
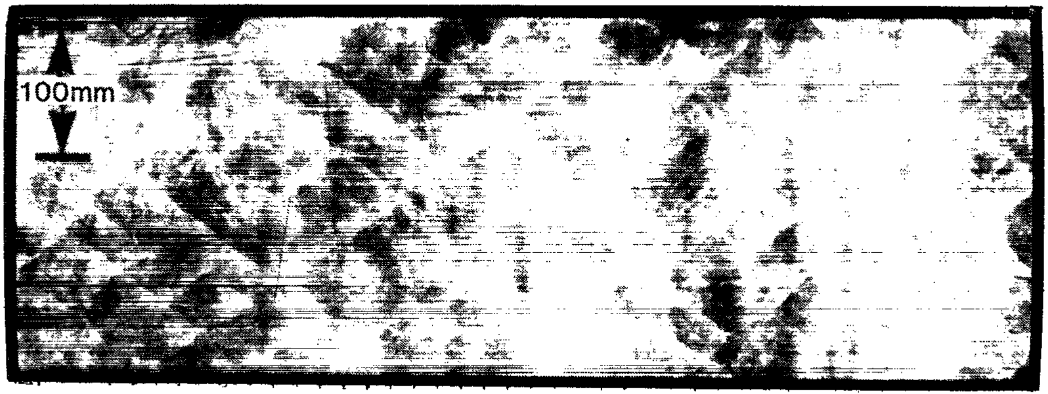
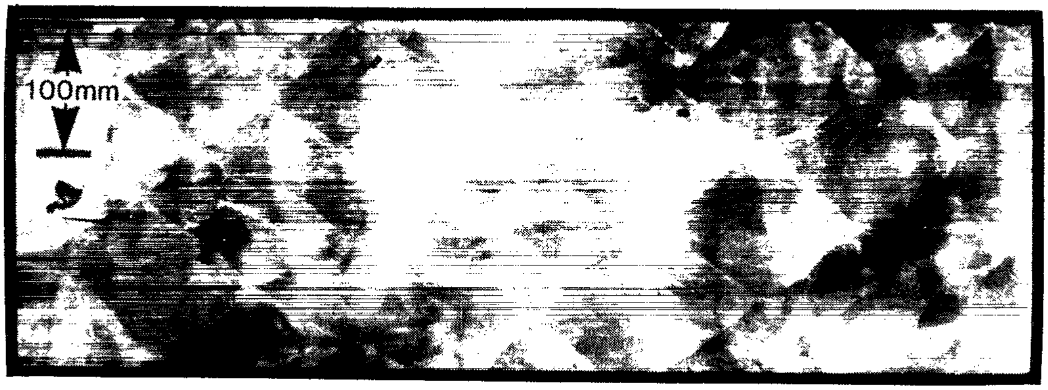


Figure 7. HYDROGEN SULPHIDE

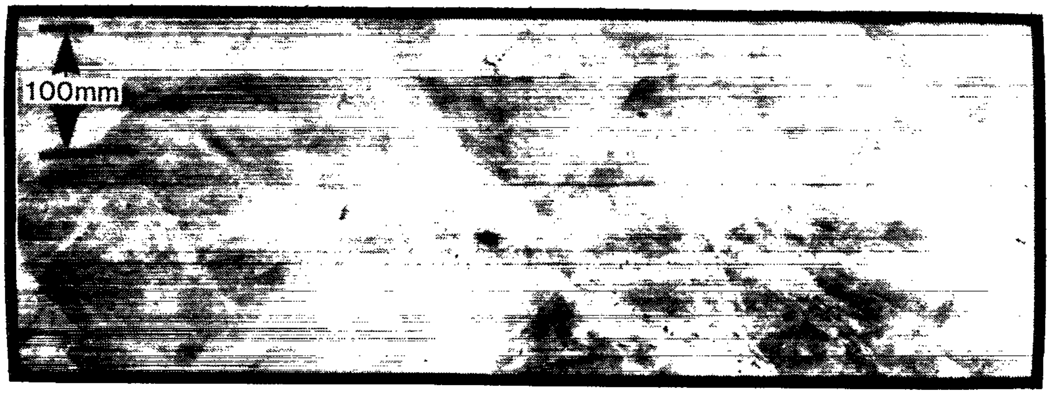


BUTANE - 3.16% S ~ 55 mm

84-178



HYDROGEN SULPHIDE - 14.2% S ~ 110 mm



HYDROGEN SULPHIDE - 10.0% S ~ 275 mm

Figure 8. COMPARISON OF CELL STRUCTURES

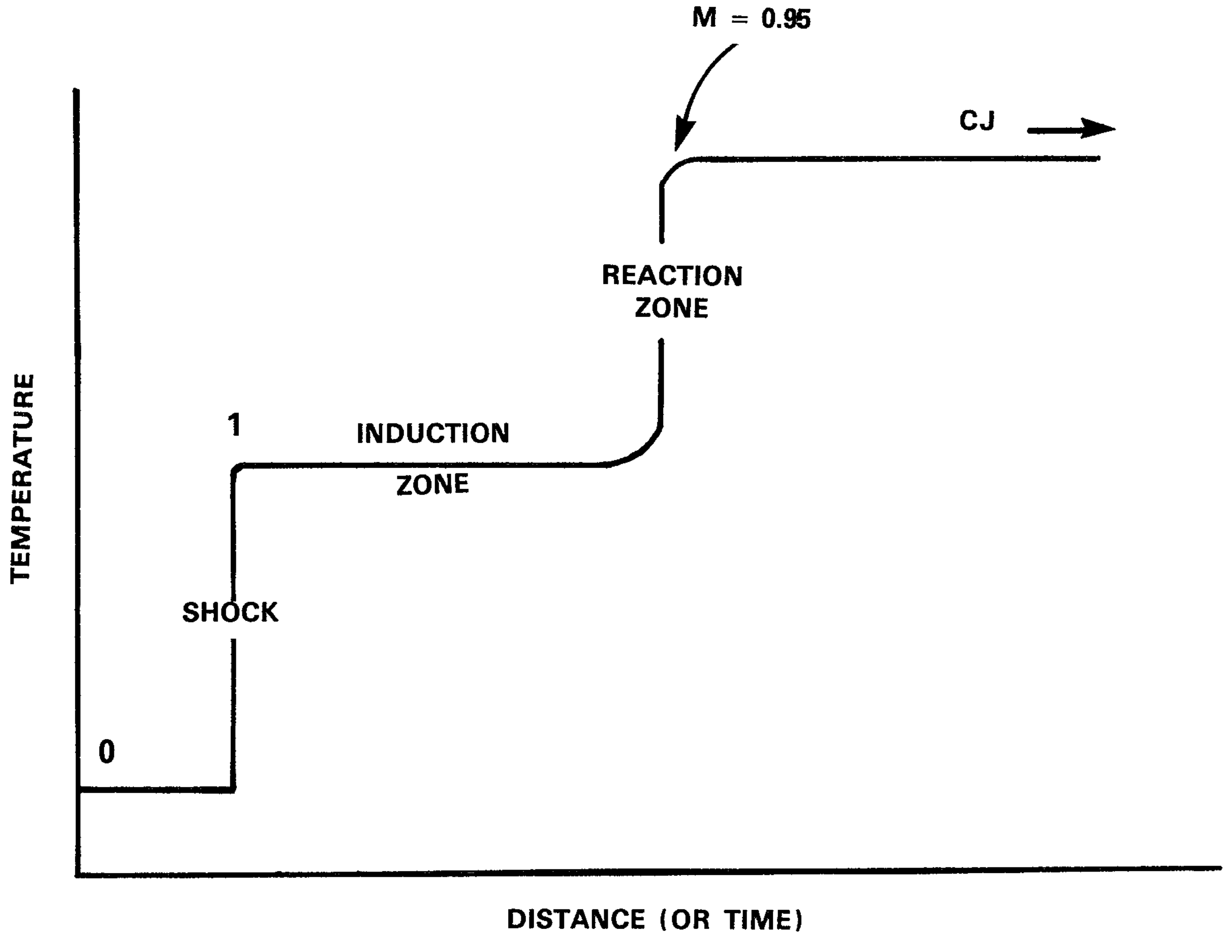


Figure 9. TEMPERATURE PROFILE IN THE ZND MODEL OF A DETONATION

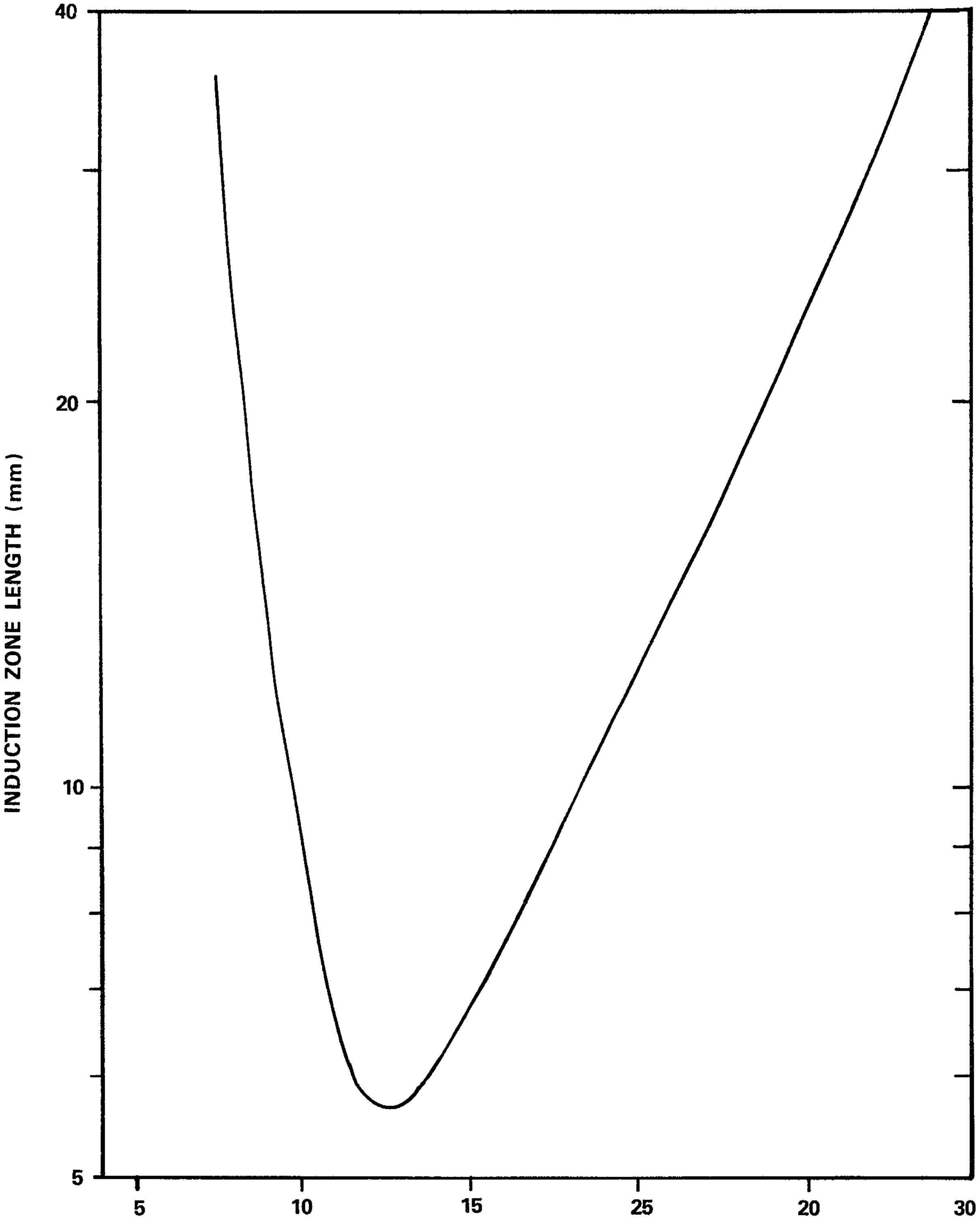

40
20
10
5
INDUCTION ZONE LENGTH (mm)
5
10
15
25
20
30
% H_2S (BY VOLUME)

FIGURE 10

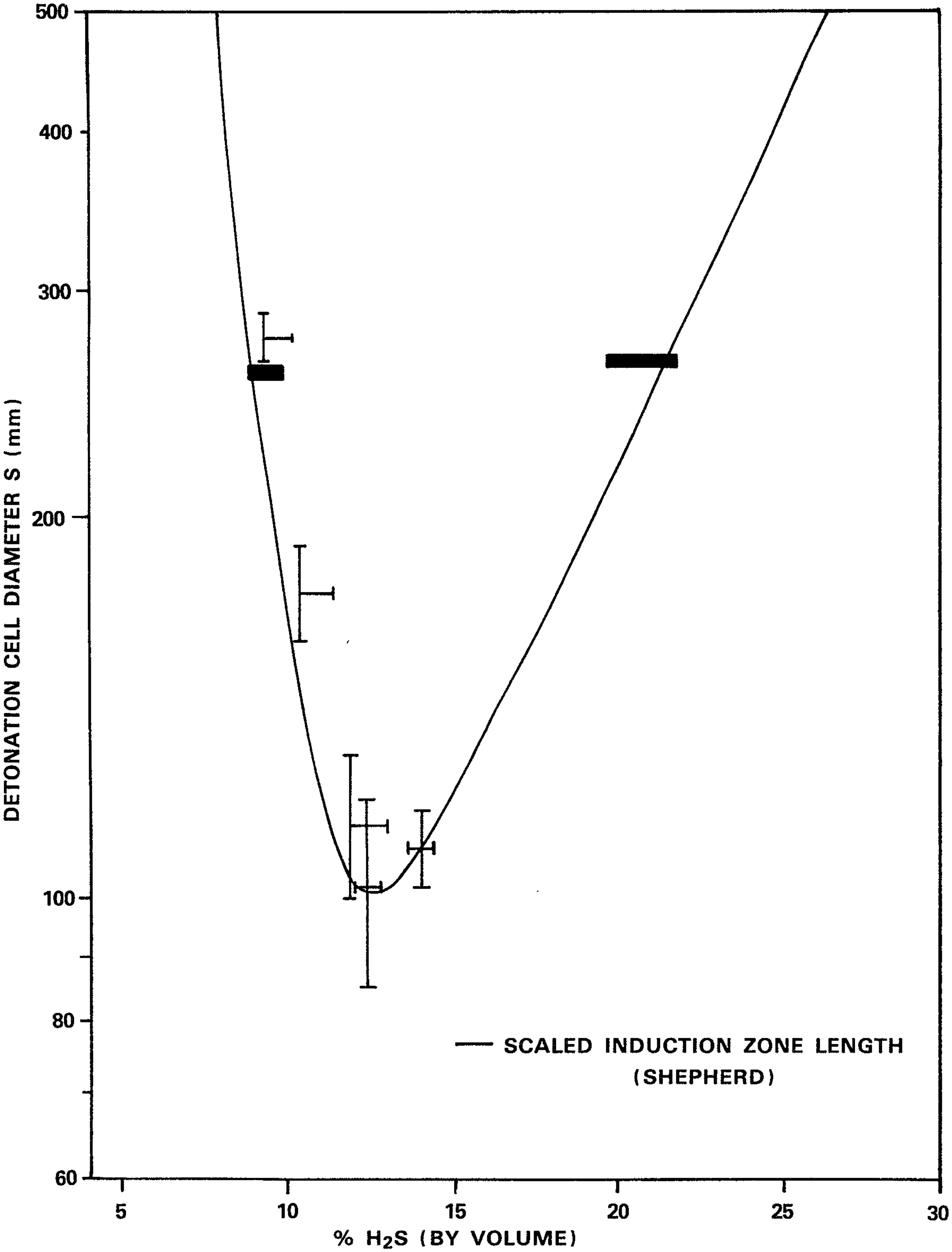

500
400
300
200
100
80
60
DETONATION CELL DIAMETER S (mm)
5
10
15
20
25
30
% H_2S (BY VOLUME)
SCALED INDUCTION ZONE LENGTH (SHEPHERD)

FIGURE 11

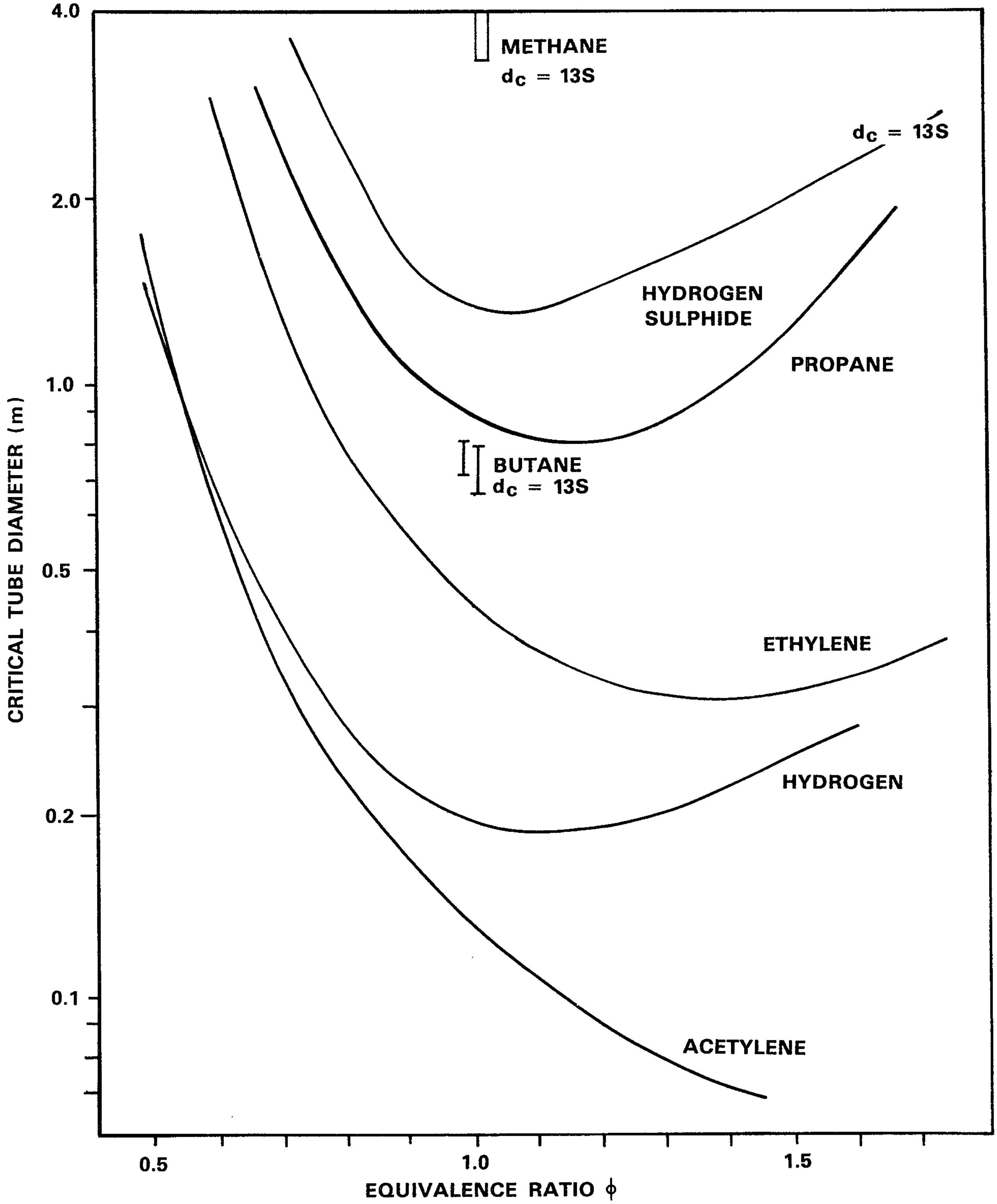

4.0
2.0
1.0
0.5
0.2
0.1
CRITICAL TUBE DIAMETER (m)
METHANE
d_c = 13S
d_c = 13S
HYDROGEN
SULPHIDE
PROPANE
BUTANE
d_c = 13S
ETHYLENE
HYDROGEN
ACETYLENE
0.5
1.0
1.5
EQUIVALENCE RATIO φ

FIGURE 12

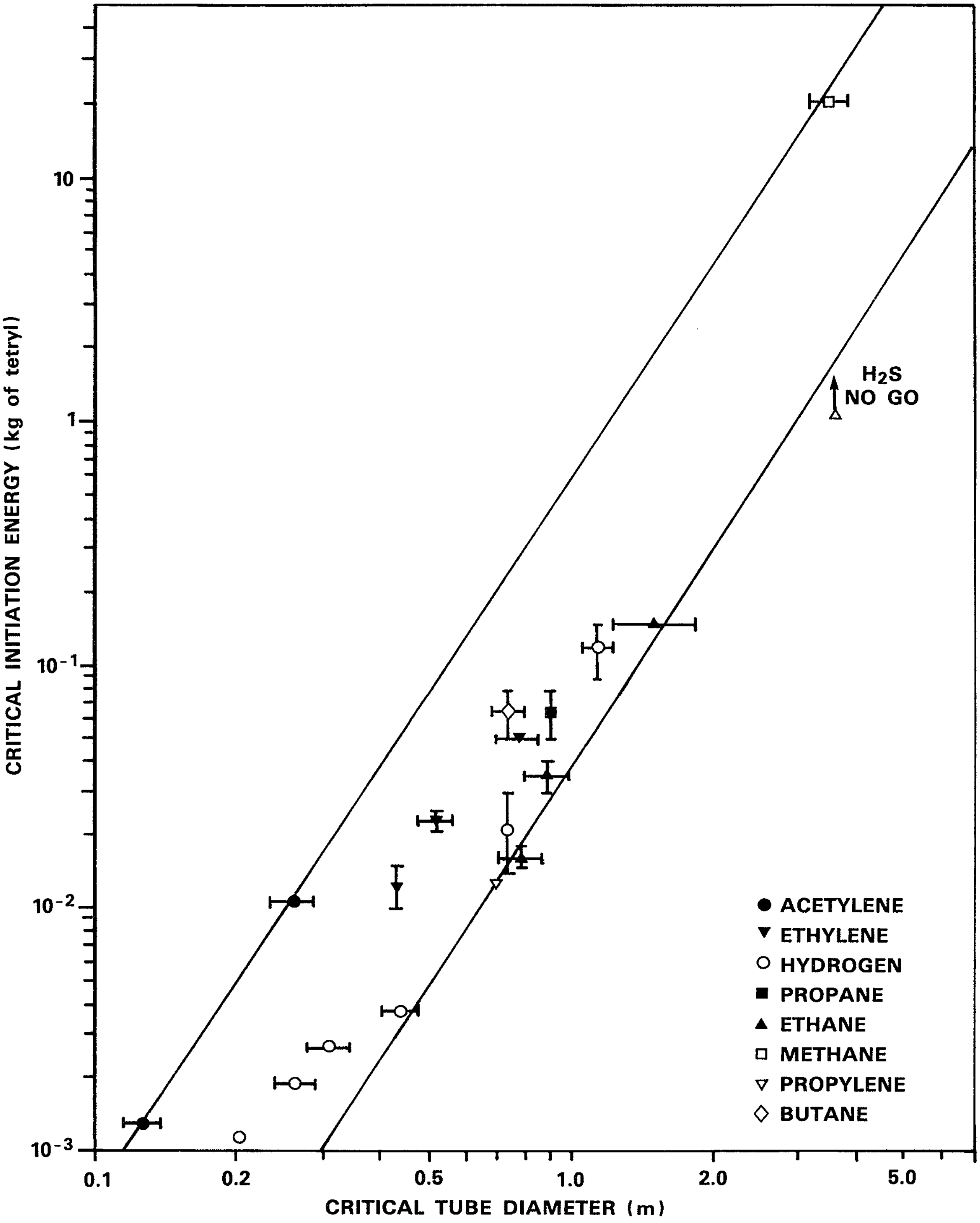

CRITICAL INITIATION ENERGY (kg of tetryl)
10
1
10^{-1}
10^{-2}
10^{-3}
0.1
0.2
0.5
1.0
2.0
5.0
CRITICAL TUBE DIAMETER (m)
H_2S
NO GO
● ACETYLENE
▼ ETHYLENE
○ HYDROGEN
■ PROPANE
▲ ETHANE
□ METHANE
▽ PROPYLENE
◇ BUTANE

FIGURE 13

APPENDIX A

SAFETY PROCEDURES
FOR
HYDROGEN SULPHIDE TRIALS

APPENDIX A

SAFETY PROCEDURES FOR HYDROGEN SULPHIDE TRIALS

Hydrogen sulphide and the product of combustion, sulphur dioxide, are highly toxic gases. A comprehensive safety plan was therefore necessary in order to ensure safety for all personnel.

In order that everyone involved with the trials became familiar with hydrogen sulphide, a specially tailored Hydrogen Sulphide Safe Handling Program was given. The course was prepared and taught by Bryne F. Emeneau of the A.E.C.L. Port Hawksbury Heavy Water Plant. The course material consisted of i) the physical and toxicological properties of hydrogen sulphide (Tables A-I and A-II show the exposure effects of H_2S and SO_2 respectively), ii) familiarization and proper care of related safety equipment such as self-contained breathing apparatus, resuscitators, and various H_2S concentration monitoring devices, and iii) hands-on training of various resuscitative techniques such as CPR, artificial respiration, and aid to a choking victim. Special procedures particular to the FAE trials were also formulated and discussed.

Since the effects of a leak of any toxic gas are severely compounded in an enclosed environment, the use of the fuel flow control trailer was not suitable. In its place, an outdoor control station was built. The station centered around a large tent which housed the flow control and monitoring equipment. During trials, the front and rear panels of the tent were removed in order to allow for complete and continuous ventilation of the area.

Numerous types of safety equipment were used during the hydrogen sulphide FAE tests. Available to personnel directly involved with the trials were six self-contained breathing apparatus with spare bottles and four escape masks with hydrogen sulphide cannisters. Monitoring equipment included two electronic H_2S detectors, two sampling tube detectors for both H_2S and SO_2, lead acetate tape for connector leak detection as well as lead acetate ampoules which were worn by all trial personnel. A medical officer equipped with resuscitative equipment was also present for each trial involving hydrogen sulphide.

In order to determine the possible downwind concentrations of H_2S if a substantial leak in the setup was to occur, dispersion calculations of H_2S as well as SO_2 were performed. The results of these calculations are summarized in Tables A-III and A-IV. Based on these calculations, a safety zone of 5 km radius was established. Only personnel aware of procedures during an emergency were allowed inside the safety zone during trials involving H_2S. Also, due to the close proximity of several other test sites ($\leqslant$ 1 km), H_2S trials could only be conducted when wind direction and speed were within strict limits. As an added safety feature, a large air-horn was installed in order to warn personnel within the safety zone that a hazardous wind change coupled with an H_2S leak had occurred.

Procedures and guidelines were developed for specific phases of the trials. These included post-trial procedures, abort procedures and emergency procedures. Also, prior to each trial, equipment checks (including checks of self-contained breathing apparatus, monitoring equipment, flow lines, etc.) were performed to ensure everything was in proper working order. Finally, all personnel were informed over open radio when flow of H_2S began and also when the area was deemed clear after a trial.

Since all trial personnel were familiar with H_2S prior to the tests, and also due to the precautions taken, the use of hydrogen sulphide did not create any particular hazard.

Table A-I

TOXICITY TABLE
FOR HYDROGEN SULPHIDE (H_2S)

---

1 PPM = 0.0001% (1/10,000 of 1%)	Can Smell
10 PPM = 0.001% (1/1,000 of 1%)	Allowable for 8 hours Exposure Threshold Limit Value (T.L.V.)

If the Level is Above 10 PPM, Then Protective Equipment Must be Worn

100 PPM = 0.01% (1/100 of 1%)	Kills Smell in 3 to 15 minutes Irritation of Eyes and Throat
200 PPM = 0.02% (2/100 of 1%)	Kills Smell Rapidly Burns Eyes and Throat
500 PPM = 0.05% (5/100 of 1%)	Loses Sense of Reasoning and Balance Stoppage of Breathing in 2 to 15 minutes Victim Needs Artificial Respiration
700 PPM = 0.07% (7/100 of 1%)	Unconscious Quickly Breathing will Stop and Death Results Unless Rescued Immediately
1000 PPM = 0.1% (1/10 of 1%)	Unconscious at Once Brain Damage Unless Rescued Promptly

1% = 10,000 PPM

PPM — Parts of Gas per Million Parts of Air by Volume

Table A-II

TOXICITY TABLE
FOR SULPHUR DIOXIDE (SO_2)

3 – 5 PPM = 0.0003 – 0.0005%	Can Smell (Rotten Eggs)
5 PPM = 0.0005%	Allowable for 8 hours Exposure Threshold Limit Value (T.L.V.)

If the Level is Above 5 PPM, Then Protective Equipment Must be Worn

20 PPM = 0.002%	Coughing and Irritation of Eyes
1000 PPM = 0.1%	Lethal Concentration Concentration that will Cause Death with Short-Term Exposure

1% = 10,000 PPM

PPM — Parts of Gas per Million Parts of Air by Volume

Table A-III

DOWNWIND CONCENTRATION OF H_2S

CONDITIONS:

12% H_2S in 20 m^3 ($\sim$ 3 kg)
15 kph Wind

DISTANCE	CONCENTRATION	
	Neutral Atmosphere Stability	**Mild Inversion**
150 m	3500 mg/m^3 or 2300 ppm	7358 mg/m^3 or 4900 ppm
1 km	123 mg/m^3 or 80 ppm	193 mg/m^3 or 130 ppm
5 km	9.3 mg/m^3 or 6 ppm	20 mg/m^3 or 13 ppm

Calculations were done by S.B. Mellsen, Chemistry Section;
DRES 3613E-1 (Chem), Memorandum Dated 21 March, 1984.
Concentrations Shown Represent Upper Limits

Table A-IV

DOWNWIND CONCENTRATION OF SO_2

CONDITIONS:

Combustion Product from 3 kg H_2S in Air

$$H_2S + \frac{3}{2}(O_2 + 3.76\ N_2) \rightarrow H_2O + SO_2 + 5.64\ N_2$$

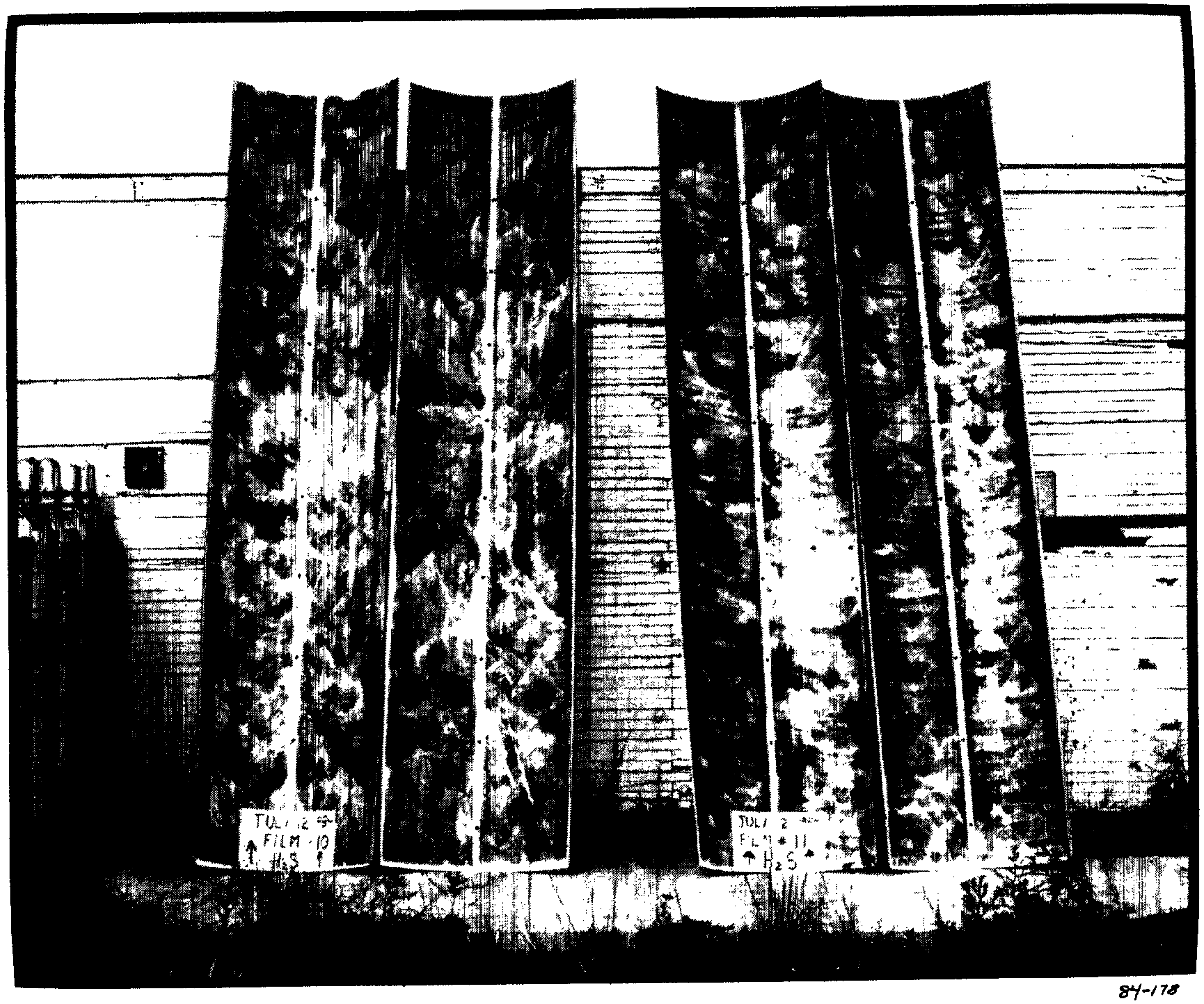
Reaction of 3 kg H_2S Produces about 6 kg SO_2
15 kph Wind

DISTANCE	CONCENTRATION	
	Neutral Atmosphere Stability	Mild Inversion
150 m	5800 mg/m³ or 2300 ppm	12200 mg/m³ or 4900 ppm
1 km	190 mg/m³ or 80 ppm	320 mg/m³ or 130 ppm
5 km	16 mg/m³ or 6 ppm	33 mg/m³ or 13 ppm

Calculations were done by S.B. Mellsen, Chemistry Section;
DRES 3613E-1 (Chem), Memorandum Dated 19 April, 1984.
Concentrations Shown Represent Upper Limits

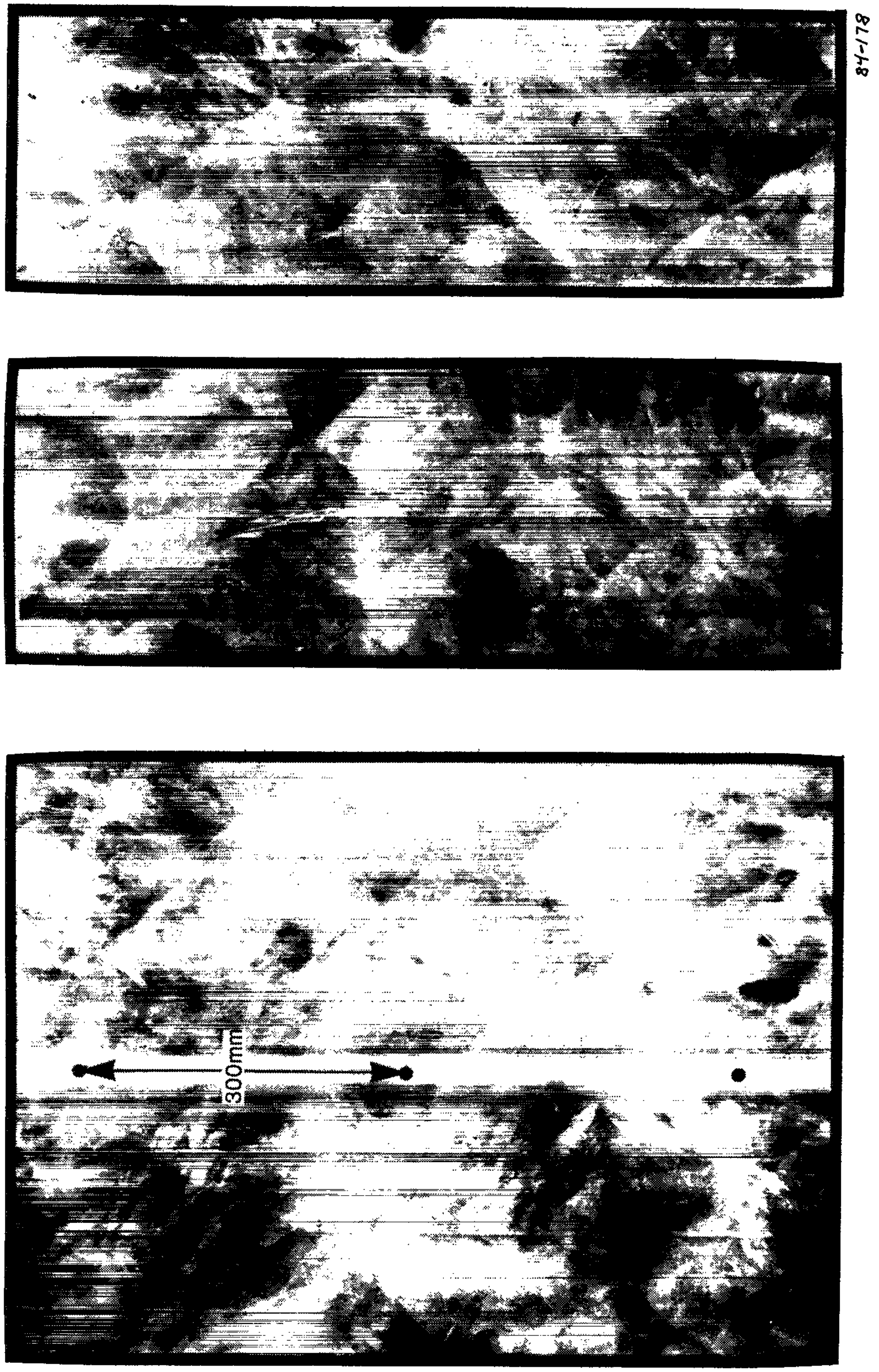
APPENDIX B

CELL STRUCTURE RECORDS

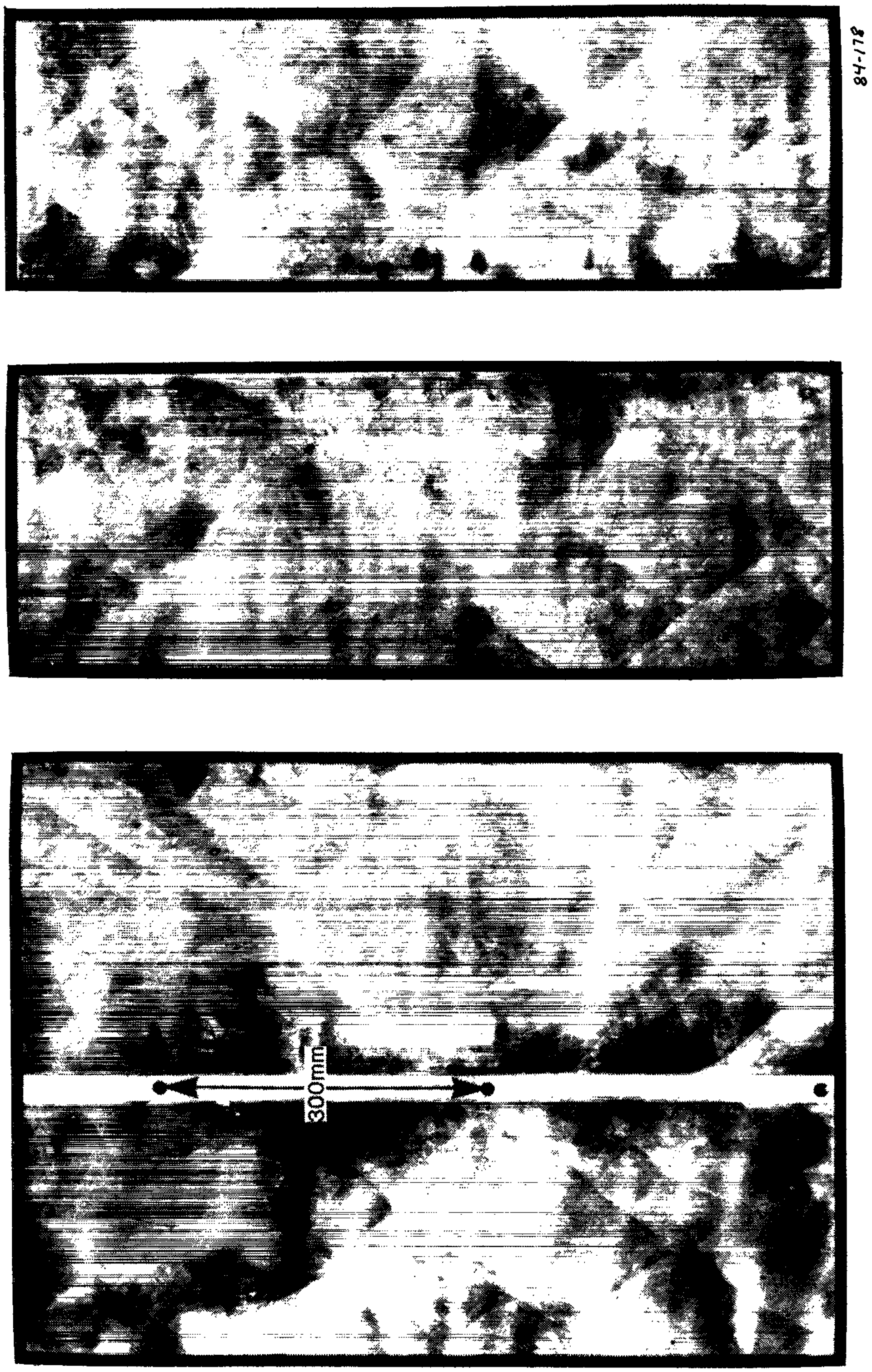


84-178

TRIALS # 10 AND # 11: SMOKED FOIL RECORDS
9.6% — 10.3% H_2S 10.5% — 11.4% H_2S



TRIAL # 10: CELL STRUCTURE
9.6% — 10.3% H_2S S ~ 275 mm

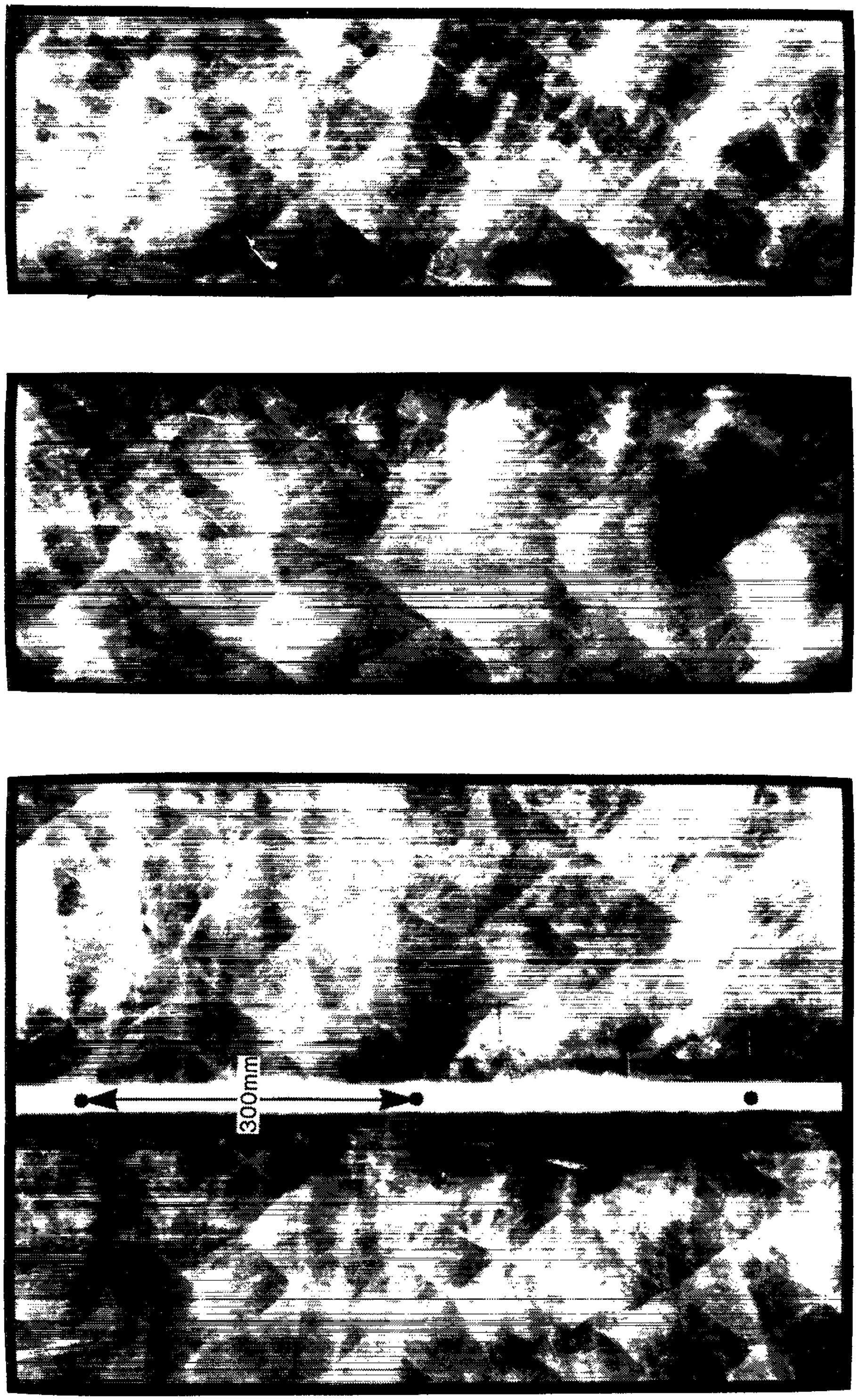


TRIAL # 11: CELL STRUCTURE
10.5% — 11.4% H_2S S ~ 175 mm

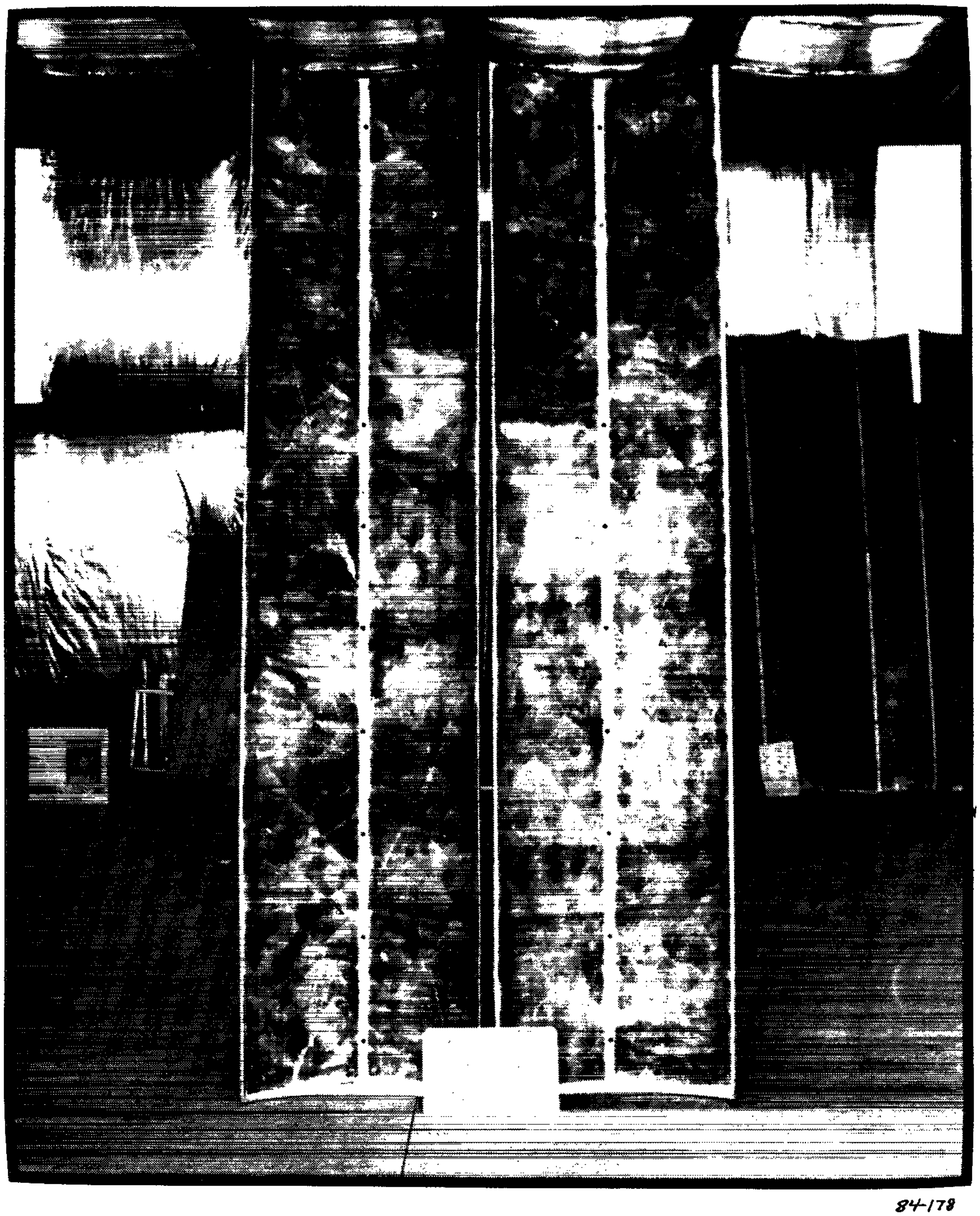
84-178

TRIAL # 12: SMOKED FOIL RECORD
12.0% – 13.2% H_2S

84-178

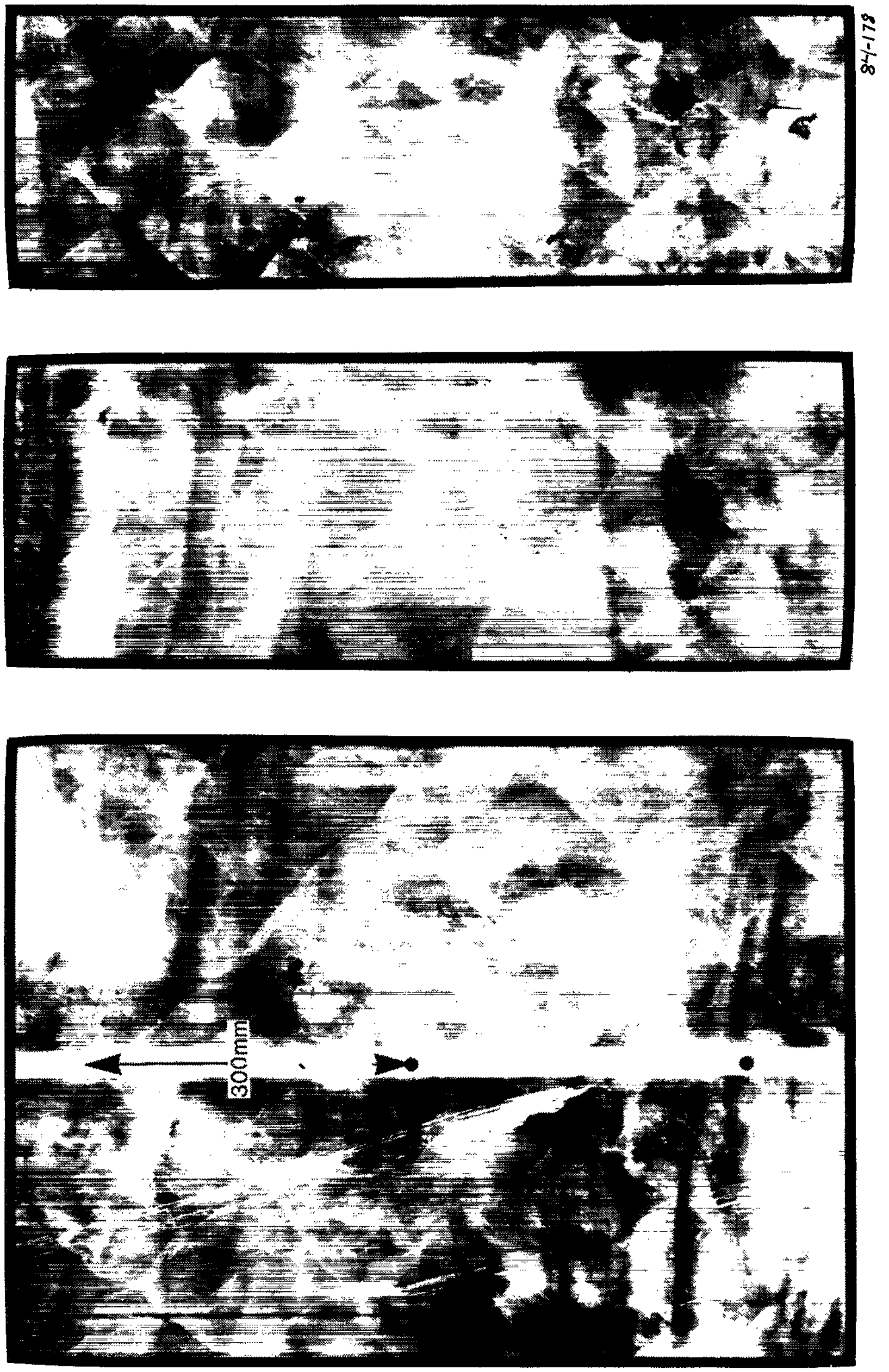


TRIAL # 12: CELL STRUCTURE
12.0% — 13.2% H_2S S ~ 115 mm



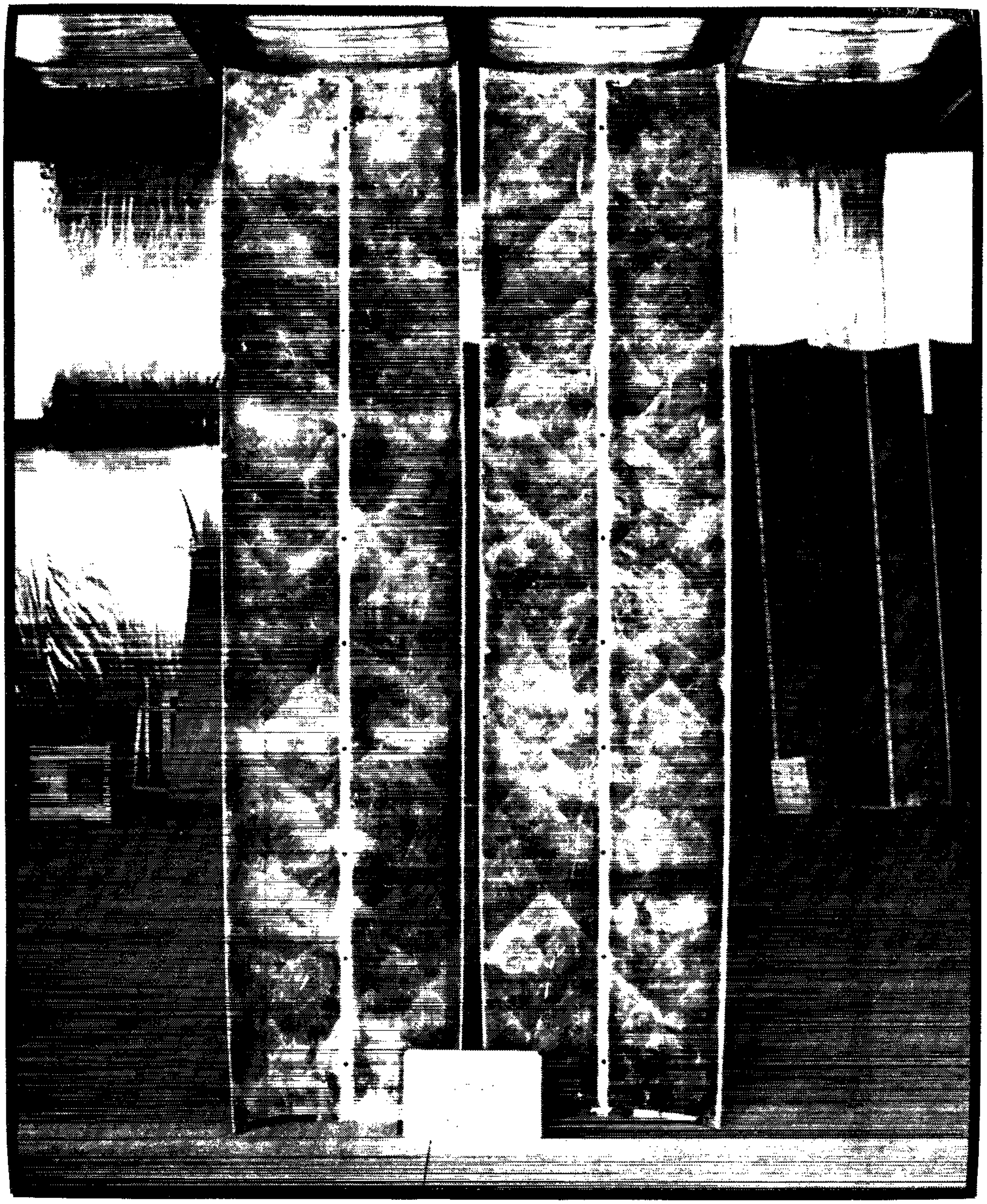
84-178

TRIAL # 26: SMOKED FOIL RECORD
13.9% — 14.5% H_2S



TRIAL # 26: CELL STRUCTURE

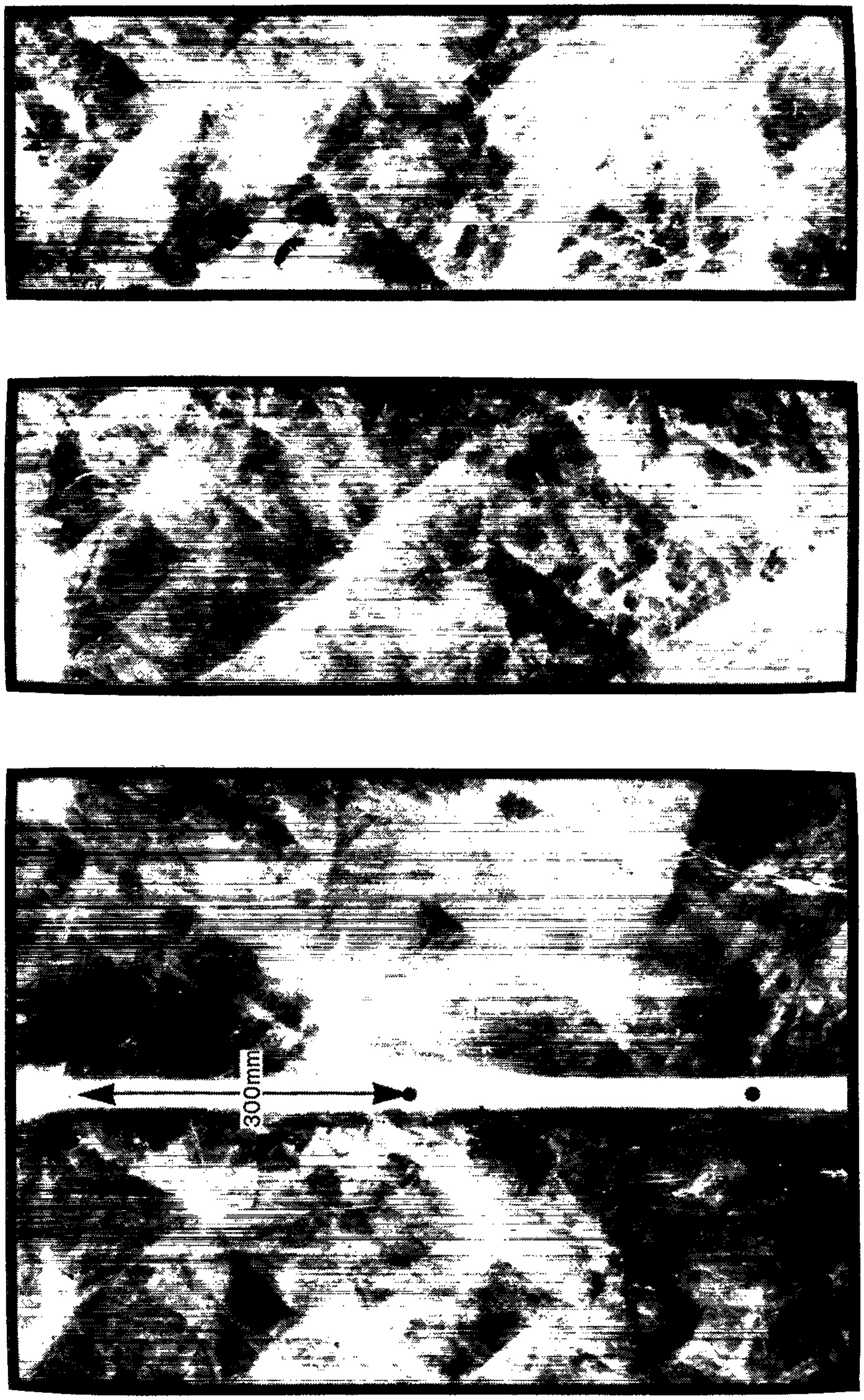
13.9% — 14.5% H_2S S ~ 110 mm



84-178

TRIAL # 29: SMOKED FOIL RECORD
12.4% – 12.8% H_2S

84-178



TRIAL # 29: CELL STRUCTURE
12.4% — 12.8% H_2S S ~ 100 mm

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DOCUMENT CONTROL DATA – R & D

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1 ORIGINATING ACTIVITY Defence Research Establishment Suffield	2a. DOCUMENT SECURITY CLASSIFICATION Unclassified 2b. GROUP
3 DOCUMENT TITLE Detonations in Hydrogen Sulphide-Air Clouds	
4 DESCRIPTIVE NOTES (Type of report and inclusive dates) Technical Report	
5. AUTHOR(S) (Last name, first name, middle initial) Sulmistras, Albert; Moen, Ingar O.; and Saber, A. Jaan	
6. DOCUMENT DATE May 1985	7a. TOTAL NO. OF PAGES 59 7b. NO. OF REFS 30
8a. PROJECT OR GRANT NO. 77C50	9a. ORIGINATOR'S DOCUMENT NUMBER(S) Suffield Memorandum No. 1140
8b. CONTRACT NO.	9b. OTHER DOCUMENT NO.(S) (Any other numbers that may be assigned this document)
10. DISTRIBUTION STATEMENT Unlimited Distribution	
11. SUPPLEMENTARY NOTES	12. SPONSORING ACTIVITY Atomic Energy Control Board of Canada Ottawa, Canada K1P 5S9

13. ABSTRACT

This paper reports on an investigation to determine the detonation hazards of hydrogen sulphide/air mixtures in relation to the detonation hazards of other more common fuel-air mixtures. Parameters which characterize the sensitivity of fuel-air mixtures to detonation are discussed. Theoretical and empirical relations between the various detonation parameters are also described, and the current status of detonation hazard evaluation is summarized. Finally, the results from a series of hydrogen sulphide/air field trials are used together with previous results and numerical calculations to determine the sensitivity of this mixture to detonation. It is found that hydrogen sulphide forms a mixture with air that is less sensitive to detonation than most common gaseous hydrocarbon fuels except methane.

This Sheet Security Classification

KEY WORDS

Explosions, Detonations, Fuel-Air Explosions, Hydrogen-Sulphide, Detonation Structure, Critical Tube, Critical Energy, Hazard Evaluation, Detonation Parameters

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